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The electronic structure of the ozone molecule

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With 3 figures in the text

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Summary

A theoretical investigation of the electronic structure of the ozone molecule has been made by the molecular orbital method, based on self-consistent linear combinations of atomic orbitals. The dissociation energy, the dipole moment of the ground state and the transitions to the lowest excited levels have been computed. All computations have been carried out in different approximations, in the simplest case considering only $2p\bar{\pi}$-electrons, in the next approximation considering all the $2p$-electrons and in the most accurate treatment considering all $2s$- and $2p$-electrons. It is found that the $2p\bar{\pi}$- and the $2s,2p$-approximations give more reliable results than the $2p$-approximation. Energy levels, ionization potentials and transition probabilities are rather similar according to the $2p\bar{\pi}$- and the $2s,2p$-approximations, but dipole moment and details of the electron distribution as given by population analysis are quite different in the different approximations.

The results of the computations in the $2s,2p$-approximation agree comparatively well with experiments. The excellent agreement between computed and experimental dissociation energy is, however, believed to be fictitious, as inclusion of $1s$-electrons will possibly change the energy values by several electron volts. The computed dipole moment has the expected sign and approximately the correct magnitude. Computed electron transitions have been tentatively assigned to observed absorption bands.

Preliminary reports of some results of the present investigation have been published in February 1955 [18] and communicated at the Molecular Quantum Mechanics Conference in Texas, December 1955.

A. Introduction

The electronic structures and spectra of triatomic molecules have been discussed previously by Mulliken [1]. Recently, Walsh [2] has also studied this subject as part of an investigation of polyatomic molecules. Finally, Moffitt [3] has made a detailed discussion of the ground state of sulphur dioxide as part of an investigation of the sulphur–oxygen bond. All these authors have used general arguments to make it plausible that the molecules have the suggested electronic structures. The structures proposed by the different authors have many similarities, but they are somewhat different with regard to the characteristics of the one-electron orbitals and the general scheme of the orbital energies. It seemed therefore to be of some interest to make a more detailed computation of the electronic structure of these molecules. The aim of the present investigation is to make a purely theoretical determination of the electronic structure of the ground state of ozone using no experimental parameters except the interatomic distances. A preliminary discussion of the lowest excited levels will also be given.

Recently [4, 5], it has been universally accepted that the three oxygen atoms of the ozone molecule form an obtuse, isosceles triangle, the shortest O–O distance being 1.278 ± 0.003 Å and the apex angle $116°49' \pm 30'$. Thus, the steric structure of ozone is very similar to those of NO_2, SO_2, ClO_2, and other dioxides of elements from the sixth and seventh groups. As the S and O atoms have similar electronic structures, a comparison between SO_2 and O_3 suggests itself. The most probable structural formulae of these oxides are shown in Fig. 1. According to Moffitt [3] the structures I and III should contribute about equally to the structure of SO_2. The double bonds of III originate from a four-valent state of the sulphur atom including $3d$ orbitals. A corresponding valence state of the apex oxygen atom of O_3 has obviously much lower probability. It has therefore been suggested [6] that the structures I and II (two of each) should give an adequate description of O_3. The experimental values of bond energies and bond lengths indicate that the S–O bond should be classified as essentially a double bond, whereas the O–O bond in O_3 is intermediate between a single and a double bond. The electric dipole moment of O_3, 0.58 Debye, is smaller than that of SO_2, 1.60 Debye, although the structure III represents a smaller moment than I. The experimental values are, however, easily understood, when it is remem-

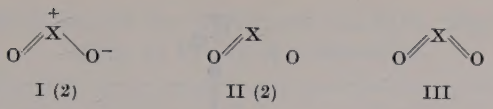

Fig. 1. Structure formulae of molecules XO_2.

bered that O is much more electronegative than S. The suggested formulae of SO_2 and O_3 are, therefore, consistent with what is known from experiments about both the bonds and the dipole moments of the molecules.

The present paper presents an investigation of the ground state of ozone according to the molecular orbital (MO) method in the linear combination of atomic orbitals (LCAO) approximation. Section B1 contains a classification of the possible wave functions and the choice of the representations of the atomic orbitals and the symmetry orbitals. Section B2 includes a discussion of the previously proposed electron configurations and the electron configurations considered in the present investigation. Section B3 deals with the choice of suitable atomic orbitals. Section B4 summarizes the energy calculation from self-consistent field MO's in the LCAO approximation. Section B5 summarizes the population analysis according to Mulliken. Section B6 outlines the calculations concerning the excited states. The Sections C present the results of the calculations and a discussion with reference to experiments and previous investigations. The Appendix D contains some details of the calculations and numerical values of some of the more than one thousand basic integrals.

B. General methods of calculation

B1. *Orbital representations*

The ozone molecule belongs to the symmetry group C_{2v}, i.e., the molecule has a two-fold symmetry axis (z-axis) and two planes of symmetry containing this axis, namely the plane of the molecule (yz-plane) and a perpendicular plane (xz-plane). The notation of the different symmetry species according to Herzberg [8] is reproduced in Table 1. (In the notation of refs. [1]–[3] b_1 and b_2 are interchanged as compared with Herzberg.)

As ozone does not show any paramagnetism originating from the electronic structure [5, 9], there are only closed shells in the ground state of the molecule, and the total electronic eigenfunction Ψ must belong to the species A_1. As usual, Ψ will be expressed as products of one-electron functions belonging to any of the species a_1, a_2, b_1 or b_2. As the aim is to find a Ψ that in the first approximation can be written

Table 1. Character table of the symmetry group C_{2v}.

C_{2v}	I	$C_2(z)$	$\sigma_v(yz)$	$\sigma_v(xz)$
A_1, a_1	+1	+1	+1	+1
A_2, a_2	+1	+1	−1	−1
B_1, b_1	+1	−1	+1	−1
B_2, b_2	+1	−1	−1	+1

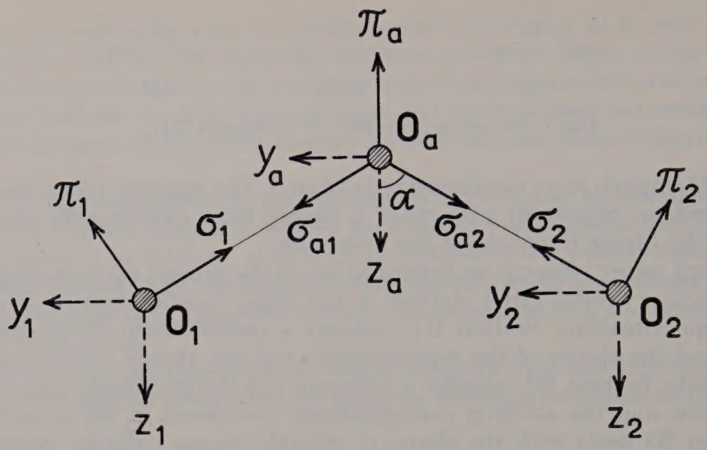

Fig. 2. Notations of atoms and of axes and corresponding AO's for the ozone molecule.

as a single, antisymmetrized product, the one-electron functions must be molecular orbitals (MO's). Furthermore, the MO's should be expressed as linear combinations of atomic orbitals (LCAO-approximation).

In the present case, it is assumed that the $1s$-electrons are completely localized and, consequently, only the AO's of the valence shell are used in the LCAO MO's ($2s,2p$-approximation). Since each oxygen atom has six electrons in the L shell, Ψ should be composed of nine, doubly filled MO's. Calculations have also been carried out with the assumption that the $2s$-orbitals are non-bonding and can be treated separately ($2p$-approximation). In this case Ψ has been composed of three MO's obtained from $2s$ AO's and six MO's obtained from $2p$ AO's. Finally, some calculations have been made in an approximation corresponding to the usual treatment of molecules with conjugated double bonds. This is denoted the $2p\bar{\pi}$-approximation. In this case, all the a_1 and b_1 electrons ($\bar{\sigma}$-electrons) have been supposed to have the same distribution as in the valence states of the atoms (see (10) and (11) in Section B2), and only the a_2 and b_2 MO's have been varied.

The notation used for the $2s$ and $2p$ AO's is as follows. The $2p$ AO's are chosen as three equivalent orbitals with mutually perpendicular axes of quantization and are denoted x, y, z. The $2s$ AO's are denoted s. The AO's of the apex atom, O_a, are distinguished by the suffix a, and the AO's of the two equivalent atoms, O_1 and O_2, by the suffixes 1 and 2.

The atomic orbitals can be combined to symmetry orbitals that are eigenfunctions of the symmetry operators of C_{2v}. Omitting the normalizing factors in the notation, the symmetry orbitals can be written:

$$\left.\begin{array}{llllll}
a_1: & s_1+s_2, & s_a, & z_1+z_2, & z_a, & y_1-y_2; \\
b_1: & s_1-s_2, & & z_1-z_2, & & y_1+y_2, \quad y_a; \\
b_2: & x_1+x_2, & x_a; & & & \\
a_2: & x_1-x_2. & & & &
\end{array}\right\} \quad (1)$$

Table 2. Transformation matrix for the two sets of AO's. The values in parenthesis apply to the $2p$-approximation.

	s_1	z_1	y_1	x_1	s_a	z_a	y_a	x_a
s_1	$+1$	0	0	0				
σ_1	0	$-\cos\alpha$	$-\sin\alpha$	0		0		
π_1	0	$-\sin\alpha$	$+\cos\alpha$	0				
$\bar{\pi}_1$	0	0	0	$+1$				
π_a					$-1/\sqrt{3}\,(+1)$	$-\sqrt{2}/\sqrt{3}\,(0)$	0	0
σ_{a1}			0		$-1/\sqrt{3}\,(0)$	$+1/\sqrt{6}\,(+1/\sqrt{2})$	$+1/\sqrt{2}\,(+1/\sqrt{2})$	0
σ_{a2}					$-1/\sqrt{3}\,(0)$	$+1/\sqrt{6}\,(+1/\sqrt{2})$	$-1/\sqrt{2}\,(-1/\sqrt{2})$	0
$\bar{\pi}_a$					0	0	0	$+1$

As the MO's also shall be eigenfunctions of C_{2v}, each MO should be composed only of the symmetry orbitals belonging to a single species. The number of MO's that can be obtained from the L shell AO's is the same as the number of symmetry orbitals, namely 5 of the species a_1, 4 of b_1, 2 of b_2 and 1 of a_2. In the following the MO's will be denoted $1a_1$, $2a_1$, …, $5a_1$, $1b_1$, … .

For the discussion of bond properties it is more convenient to transform the orbitals to another set of basic AO's. Let σ_{a1}, σ_{a2} and π_a be three equivalent orbitals obtained by combination of s_a, y_a and z_a and directed as indicated in Fig. 2. Furthermore, let σ_1, π_1 and $\bar{\pi}_1$ denote $2p$ orbitals, σ_1 with its axis in the bond direction, π_1 with its axis perpendicular to this direction but in the molecular plane, and $\bar{\pi}_1$ with its axis perpendicular to this plane (cf. Fig. 2). In the $2p$-approximation π_a is replaced by s_a, and σ_{a1} and σ_{a2} are equivalent combinations of y_a and z_a. The matrix of the transformation from the $x, y, z \ldots$ set of AO's to the $\sigma, \pi, \bar{\pi} \ldots$ set is given in Table 2, where the matrix elements in parenthesis apply to the $2p$-approximation.

The symmetry orbitals of the second representation are:

$$\left.\begin{aligned}
&a_1\colon\ s_1+s_2,\ \sigma_1+\sigma_2,\ \sigma_{a1}+\sigma_{a2},\ \pi_1+\pi_2,\ \pi_a;\\
&b_1\colon\ s_1-s_2,\ \sigma_1-\sigma_2,\ \sigma_{a1}-\sigma_{a2},\ \pi_1-\pi_2;\\
&b_2\colon\ \bar{\pi}_1+\bar{\pi}_2,\ \bar{\pi}_a;\\
&a_2\colon\ \bar{\pi}_1-\bar{\pi}_2.
\end{aligned}\right\} \qquad (2)$$

Sometimes it is desirable to distinguish between different molecular orbitals belonging to the same species. Then the symbol of the correlated orbital in a linear molecule can be added [1], [2], e.g. $a_1\sigma_g$.

B 2. *Electron configurations*

The following electron configurations, where the orbitals are given in order of increasing orbital energy,

$$(a_1\sigma_g)^2(b_1\sigma_u)^2(a_1\sigma_g)^2(b_2\pi_u)^2(a_1\pi_u)^2(b_1\sigma_u)^2(a_2\pi_g)^2(a_1\sigma_g)^2(b_1\pi_g)^2 \tag{3}$$

and

$$(a_1\sigma_g)^2(b_1\sigma_u)^2(a_1\sigma_g)^2(b_2\pi_u)^2(a_1\pi_u)^2(b_1\sigma_u)^2(a_2\pi_g)^2(b_1\pi_g)^2(a_1\pi_u)^2 \tag{4}$$

have been proposed, the first by Mulliken [1] and the other by Walsh [2], for triatomic molecules with an apex angle of 120° and 18 valence electrons. The difference between (3) and (4) concerns the order of the two outermost orbitals, a_1 and b_1, and the correlation of a_1 to an orbital of a linear molecule. Moreover, the orbital energies estimated by the two authors are somewhat different. Omitting the $\sigma_g, \pi_u \ldots$ symbols and leaving open the question of the order of the outermost orbitals, (3) and (4) can be written

$$(1a_1)^2(1b_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(2b_1)^2(1a_2)^2(4a_1)^2(3b_1)^2. \tag{5}$$

(5) is also the electron configuration of SO_2 proposed by Moffitt [3], who does not discuss the order of the orbital energies at all.

Except the nine filled MO's of (5) there are three more MO's that can be formed from the valence shell AO's. According to [1] and [2] the order of these orbitals should be $2b_2$, $5a_1$, $4b_1$. The energy of the $2b_2$ orbital should be very close to the energy of the highest filled orbital. Therefore, it seemed to be of some interest to ascertain that the proposed general orbital scheme is applicable to O_3 and should not be slightly changed for this molecule. Consequently, not only (5) but also some other configurations have been investigated. As the three highest orbitals of (5), $1a_2$, $4a_1$ and $3b_1$, are supposed to be antibonding, the configurations obtained by replacing anyone of these orbitals by $2b_2$ can be expected to give comparatively low molecular energy values and have therefore also been investigated. The treated configurations are thus:

$$\Psi_1\text{:}\quad (1a_1)^2(1b_1)^2(2a_1)^2(2b_1)^2(3a_1)^2(1b_2)^2(1a_2)^2(4a_1)^2(3b_1)^2, \tag{6}$$

$$\Psi_2\text{:}\qquad \text{(same)} \qquad (4a_1)^2(3b_1)^2(2b_2)^2, \tag{7}$$

$$\Psi_3\text{:}\qquad \text{,,} \qquad (1a_2)^2(4a_1)^2(2b_2)^2, \tag{8}$$

$$\Psi_4\text{:}\qquad \text{,,} \qquad (1a_2)^2(3b_1)^2(2b_2)^2. \tag{9}$$

For calculations in the $2p$-approximation it has been assumed that the three lowest orbitals, $1a_1$, $1b_1$ and $2a_1$, are pure s-orbitals, and that the other six orbitals are pure p-orbitals.

For calculations in the $2p\bar{\pi}$-approximation, where only the a_2 and b_2 orbitals are analyzed, some assumption must be made about the valence states of the oxygen atoms. The valence states of O_1 and O_2 must be reflections, but the state of O_a is supposed to have another orientation in space than the other two. The assumed electron configurations are:

$$O_1\text{:}\quad (2s_1)^2\,(2p\pi_1)^2\,2p\,\sigma_1\,2p\,\bar{\pi}_1, \tag{10}$$

$$O_a\text{:}\quad (2s_a)^2\,(2p\,\bar{\pi}_a)^2\,2p\,\sigma_{a1}\,2p\,\sigma_{a2}. \tag{11}$$

The σ-orbitals of (11) are of course pure p-orbitals.

B 3. *Atomic orbitals*

When a calculation including superposition of many configurations is carried out, the question of the basic atomic orbitals is of minor importance. However, when the number of configurations is limited, as in the present case, the choice of atomic orbitals is a very important one. It has been pointed out several times (e.g. by the author [10] and by Sponer and Löwdin [11]) that the simple analytical atomic orbitals of the kind introduced by Slater do not agree very well with the more accurate numerical orbitals obtained by the self-consistent field method according to Hartree and Fock (SCF-orbitals). Undoubtedly, the SCF-orbitals give better results in calculations of atomic energy levels than do the analytical orbitals. Whether the same is true for molecular calculations is, however, not immediately obvious. It has been shown by Sponer and Löwdin [11] that the analytical orbitals and the SCF-orbitals will yield about the same final result in the $2p\bar{\pi}$-approximation for ethylene, although the individual integrals are markedly different. However, this result does not exhaust the comparison of the two kinds of atomic orbitals. It is a common approximation to use the same exponential in the analytical expressions of the Slater $2s$ and $2p$ orbitals. Every SCF-computation shows, however, that the $2p$ orbitals are more extended than the $2s$ orbitals. Consequently, the computation of such quantities as dipole moment and degree of hybridization should give different results using the simplest Slater orbitals and SCF-orbitals. Furthermore, the greatest error in using analytical orbitals does not originate from the electron interaction integrals, mainly depending on the extension of the orbitals. In fact, the integrals representing the nuclear-electronic interaction and the kinetic energy are more critical, since they depend mainly on the form of the orbitals in the immediate vicinity of the nuclei. These later integrals cancel in the investigation [11], which was not concerned with the energy of the ground state. It is true that some energy terms of this kind will be subtracted from the molecular energy expression when the binding energy is computed, but these terms are significant, e.g. for the determination of the degree of s,p-hybridization.

In the present investigation the best numerical SCF-orbitals of the oxygen atom [12] have been used. The results ommunicated here will in a future publication be compared with results obtained by use of simple, analytical AO's.

B 4. *Energy calculations*

The molecular orbitals have been computed by a self-consistent field procedure. This kind of molecular orbital calculation has recently been reviewed, improved and partly reformulated by Roothaan [13]. The calculation procedure of the present paper follows in principal features that of Roothaan.

Neglecting the kinetic energy of the nuclei, the Hamiltonian operator of the molecule, expressed in atomic units, is:

$$H=\sum_{t} U_t+\tfrac{1}{2}\sum_{t,u} V_{tu}+\tfrac{1}{2}\sum_{k,m} Z_k Z_m R_{km}^{-1}, \tag{12}$$

where the one-electron operator U_t is the sum of the kinetic energy of the electron and of its potential energy in the field of the nuclei and the inner shell electrons. The second sum of (12) is the inter-electronic repulsion operator, $V_{tu}=r_{tu}^{-1}$, r_{tu} being the distance between electron t and electron u. The last sum of (12) is the inter-nuclear repulsion operator. This term can be dropped in the intermediate calculations and reconsidered only in the final computation of the molecular energy.

In the Hartree-Fock approximation, where superposition of configurations is neglected, the eigenfunction Ψ of H can be written as one Slater determinant of MO's $\varphi_i(t) = |i\rangle$. In the LCAO approximation each MO can be written as a combination of symmetry orbitals $\zeta_\mu(t) = |\mu\rangle$, which are themselves combinations of AO's $\chi_r(t) = |r\rangle$, (cf. Section B1). Thus

$$\left.\begin{aligned} \varphi_i &= \sum_\mu \zeta_\mu \langle\mu|i\rangle = \sum_r \chi_r \langle r|i\rangle, \\ \text{or} \qquad |i\rangle &= \sum_\mu |\mu\rangle\langle\mu|i\rangle = \sum_r |r\rangle\langle r|i\rangle. \end{aligned}\right\} \tag{13}$$

The set of numbers $\langle\mu|i\rangle$ is the representative of the MO φ_i in the symmetry orbital representation, and the set $\langle r|i\rangle$ is the representative of φ_i in the atomic orbital representation. Using a matrix notation the numbers $\langle\mu|i\rangle$ ($\langle r|i\rangle$) are the elements of a column matrix. In order to obtain the best LCAO MO's the numbers $\langle\mu|i\rangle$ ($\langle r|i\rangle$) should be determined by a variational treatment, as described below.

The Hartree-Fock equations for the closed-shell ground state are:

$$\sum_\nu \{\langle\mu|F|\nu\rangle\langle\nu|i\rangle - \varepsilon_i \langle\mu|S|\nu\rangle\langle\nu|i\rangle\} = 0 \tag{14}$$

with similar expressions in the AO representation. **S** is the quadratic overlap matrix with the elements

$$\langle\mu|S|\nu\rangle = \langle\mu|\nu\rangle = \int \zeta_\mu^* \zeta_\nu \, d\tau.$$

F is a quadratic matrix representing the one-electron Hartree-Fock operator, and the parameters ε_i are the eigenvalues of F. The matrix elements of **F** are

$$\langle\mu|F|\nu\rangle = \langle\mu|U + 2J - K|\nu\rangle. \tag{15}$$

The operator U of (15) is the same as U_t of (12). The matrix $2\mathbf{J} - \mathbf{K}$ representing the electron interaction operator has the following elements:

$$\begin{aligned} \langle\mu|2J-K|\nu\rangle &= \sum_i \{2\int \zeta_\mu^*(t)\,\varphi_i^*(u)\,V_{tu}\,\zeta_\nu(t)\,\varphi_i(u)\,d\tau_t\,d\tau_u - \\ &\qquad - \int \zeta_\mu^*(t)\,\varphi_i^*(u)\,V_{tu}\,\varphi_i(t)\,\zeta_\nu(u)\,d\tau_t\,d\tau_u\} \\ &= \sum_{\varkappa,\lambda} \langle\varkappa|d|\lambda\rangle\{2(\mu\nu|\lambda\varkappa) - (\mu\varkappa|\lambda\nu)\} \\ &= \sum_{r,s} \langle r|d|s\rangle\{2(\mu\nu|sr) - (\mu r|s\nu)\}, \end{aligned} \tag{16}$$

where

$$\langle\varkappa|d|\lambda\rangle = \sum_i \langle\varkappa|i\rangle\langle i|\lambda\rangle, \tag{17}$$

$$\langle r|d|s\rangle = \sum_i \langle r|i\rangle\langle i|s\rangle \qquad (\langle i|s\rangle = \langle s|i\rangle^*), \tag{18}$$

and

$$(a\,b\,|\,c\,d) = \int \psi_a^*(t)\,\psi_c^*(u)\,V_{tu}\,\psi_b(t)\,\psi_d(u)\,d\tau_t\,d\tau_u. \tag{19}$$

ψ in (19) stands for any of the orbitals φ, ζ or χ. The sums over i in (16), (17), (18) and below are taken over all the filled molecular space-orbitals, and the sums over $\varkappa$, λ and r, s are taken over all pairs of basic orbitals.

The numbers $\langle r|i\rangle$ are determined by the variational principle leading to the secular determinant equation

$$\mathrm{Det}\,|\langle\mu|F|\nu\rangle - \varepsilon\langle\mu|S|\nu\rangle| = 0. \tag{20}$$

This equation is of the 12th degree in ε in the $2s$,$2p$-approximation and of the 9th degree in the $2p$-approximation. According to the symmetry (cf. Section B1) (20) factorizes into four determinants corresponding to the symmetry species a_1, b_1, b_2 and a_2. These determinants are in the $2s$,$2p$-approximation of the 5th, 4th, 2nd and 1st order and in the $2p$-approximation of the 3rd, 3rd, 2nd and 1st order. As the matrix elements $\langle\mu|F|\nu\rangle$ are functions of the $\langle r|i\rangle$'s, cf. (16)–(18), an iterative procedure must be used for the determination of the $\langle r|i\rangle$'s.

In the $2p$-approximation a satisfactory consistency was obtained after 6 or 7 cycles. In the $2s$,$2p$-approximation the convergence was considerably slower. As each cycle was rather time-consuming in this approximation, a comparatively low degree of accuracy was accepted as sufficient. In the most accurate computations, which were carried out with the wave function (6), the uncertainty in the $2p$-approximation of the $\langle r|i\rangle$'s was at worst 0.003 and of $\langle r|d|s\rangle$ 0.001. In the $2s$,$2p$-approximation the uncertainty of $\langle r|i\rangle$ was always below 0.03 and with a few exceptions below 0.01. The uncertainty of $\langle r|d|s\rangle$ was in most cases below 0.005 but in a few cases as high as 0.01.

Consider any operator M, which can be written as a sum of one-electron operators, $M = \sum_t M_t$. The expectation value $\langle M\rangle$ of M is a linear function of the numbers $\langle r|d|s\rangle$:

$$\langle M\rangle = \int \Psi^* M\,\Psi\,d\tau = 2\sum_{i,r,s}\langle i|s\rangle\langle s|M_t|r\rangle\langle r|i\rangle = 2\sum_{r,s}\langle r|d|s\rangle\langle s|M_t|r\rangle. \tag{21}$$

One operator of this kind is the electric dipole moment μ of the ground state:

$$\mu = \sum_t z_t - \sum_k Z_k z_k, \tag{22}$$

where all the coordinates z should be measured from a common origin. The second sum in (22) is taken over the nuclei.

Another operator of this kind is the total molecular energy in the Hartree-Fock approximation:

$$H = \sum_t U_t + \tfrac{1}{2}\sum_t (2\,J_t - K_t) + \tfrac{1}{2}\sum_{k,m} Z_k Z_m R_{km}^{-1}, \tag{23}$$

$$\langle H\rangle = E_{\mathrm{mol}},$$

(for the definition of the one-electron operators J_t and K_t, introduced by Dirac, cf. (16) above). Alternative expressions of E_{mol} can be given by introduction of the eigenvalues ε_i of F, cf. (14). We have

$$\sum_i \varepsilon_i = \sum_i \langle i | U + 2J - K | i \rangle = \sum_{r,s} \langle r | d | s \rangle \left[\langle s | U | r \rangle + \langle s | 2J - K | r \rangle \right], \tag{24}$$

$$\begin{aligned} E_{\text{mol}} - \tfrac{1}{2} \sum_{k,m} Z_k Z_m R_{km}^{-1} &= \sum_{r,s} \langle r | d | s \rangle \langle s | U | r \rangle + \sum_i \varepsilon_i \\ &= 2 \sum_i \varepsilon_i - \sum_{r,s} \langle r | d | s \rangle \langle s | 2J - K | r \rangle. \end{aligned} \tag{25}$$

When superposition of configurations is included, the total wave function is

$$\Psi = \sum_\lambda C_\lambda \Psi_\lambda. \tag{26}$$

Before superposing the Ψ_λ's, each Ψ_λ has been specified by a determination of the numbers $\langle r | i \rangle$ of (13) as described above. Afterwards the C_λ's have been determined by the variational principle with fixed $\langle r | i \rangle$ values. This procedure leads to a secular determinant equation of the type

$$\text{Det } \left| \langle \varkappa | H | \lambda \rangle - E \delta_{\varkappa\lambda} \right| = 0. \tag{27}$$

When all the MO's of the superposed configurations are orthogonal, the MO's of $\Psi_\varkappa$ must be the same as those of Ψ_λ with the exception of at most two MO's. Thus, when $\varkappa \neq \lambda$:

$$\int \Psi_\varkappa^* \Psi_\lambda \, d\tau = 0, \tag{29}$$

$$\int \Psi_\varkappa^* M_t \Psi_\lambda \, d\tau \neq 0, \tag{30}$$

$$\int \Psi_\varkappa^* V_{tu} \Psi_\lambda \, d\tau \neq 0. \tag{31}$$

The present investigation includes only superposition of configurations in the $2p\bar{\pi}$-approximation. The configurations used for the ground state are (6) and (7). In this case only the integral (31) $\neq 0$. The lowest root of equation (27) gives the energy of the ground state of the molecule. The next root is likely to approximate the first doubly excited energy level of the symmetry $^1A_1$.

B 5. *Population analysis*

The numbers $\langle r | d | s \rangle$ of (18) can be considered as elements of a matrix **d**, which is closely connected with the charge and bond order matrix of Coulson, Löwdin and others and with Mulliken's population numbers [7]. In the following, Mulliken's population notation will be used, but the populations are in most cases expressed by aid of the $\langle r | d | s \rangle$'s instead of by the $\langle r | i \rangle$'s, used by Mulliken.

Mulliken's subtotal, net atomic population $n(r)$ is:

$$n(r) = 2 \sum_i \langle r | i \rangle \langle i | r \rangle = 2 \langle r | d | r \rangle, \tag{32}$$

and his sub-total overlap population $n(r, t)$, which is the overlap population of the AO's χ_r and χ_t of two different atoms, is

$$n(r, t) = 4 \sum_i \langle i|r\rangle \langle r|S|t\rangle \langle t|i\rangle = 4 \langle t|d|r\rangle \langle r|S|t\rangle, \quad r \neq t. \tag{33}$$

The gross atomic population $N(r)$ of the AO χ_r is

$$N(r) = 2 \sum_{i,t} \langle i|r\rangle \langle r|S|t\rangle \langle t|i\rangle = 2 \sum_t \langle t|d|r\rangle \langle r|S|t\rangle, \tag{34}$$

where the sum over t is to be taken over all AO's including χ_r itself. The $\langle r|S|r\rangle$'s are equal to 1, as all orbitals χ, ζ and φ are normalized to 1. In (32)–(34) the sum over i should be taken over all filled molecular space-orbitals, i.e. every doubly filled MO taken once, as in the preceding section. The total gross atomic population on a single atom k is obtained by summing over all AO's χ_{r_k} of that atom:

$$N(k) = \sum_{r_k} N(r_k). \tag{35}$$

It is also of interest to consider the formal charge Q in an AO or on an atom, which is the difference between the population number $\bar{N}$ referred to the atomic valence state and the population number N referred to the molecule:

$$Q(r) = \bar{N}(r) - N(r), \qquad Q(k) = \bar{N}(k) - N(k). \tag{36}$$

$\bar{N}(r)$ and $\bar{N}(k)$ are usually integers. In the case of ozone the $\bar{N}(r)$'s are only integers in the AO representation (2). $\bar{N}(y_1)$ and $\bar{N}(z_1)$ of representation (1) are fractions. The overlap population $n(i)$ of a molecular orbital $\varphi(i)$ is:

$$n(i) = 2 \sum_{r,t}^{r \neq t} \langle i|r\rangle \langle r|S|t\rangle \langle t|i\rangle. \tag{37}$$

$n(i)$ can be split up in the overlap populations $n(i; k, m)$ between all pairs of atoms k and m:

$$n(i) = \sum_{k,m}^{k>m} n(i; k, m) = 2 \sum_{k,m}^{k>m} \sum_{r_k, t_m} \langle i|r_k\rangle \langle r_k|S|t_m\rangle \langle t_m|i\rangle. \tag{38}$$

Finally, the total overlap population n of the molecule is:

$$n = \sum_i n(i) = \sum_{r,t}^{r>t} n(r, t) = \sum_{k,m}^{k>m} n(k, m),$$

where

$$n(k, m) = 2 \sum_i n(i; k, m) = 4 \sum_{r_k, t_m} \langle t_m|d|r_k\rangle \langle r_k|S|t_m\rangle \tag{39}$$

is the total overlap population between the atoms k and m.

B 6. *Excited states*

In the present investigation only a preliminary treatment of the excited states has been carried out. As is well known, the solution of the Hartree-Fock equations

(14) yields both the filled MO's of the ground state and the unfilled MO's obtainable from $2s$ and $2p$ AO's and orthogonal to the filled MO's. The unfilled MO's are $2b_2$, $5a_1$ and $4b_1$. The electron configurations of the singly excited states have been obtained by promotion of one electron from a filled MO to one of the empty MO's, leaving all the other MO's unchanged. It could not be expected that energy values obtained from a description of the excited states by a single configuration of this kind are satisfactory. However, a comparison of the transitions calculated in the $2s$,$2p$-, $2p$- and $2p\bar{\pi}$-approximations indicates, how the results of the present calculation are likely to be changed by a more rigorous treatment, and makes it possible to correlate the electronic transitions to the observed bands of the absorption spectrum.

The energy ${}^1E_{lm}$ of an excited singlet state obtained by promotion of an electron from the MO φ_l to the MO φ_m can be obtained from the energy E_0 of the ground state as follows (cf. [13]). Using (24) and (16) the vertical ionization energy of an electron can be written

$$\begin{aligned}\varepsilon_l &= \langle l \,|\, U + 2\,J - K \,|\, l\rangle \\ &= \langle l \,|\, U \,|\, l\rangle + \sum_i \{2\,\langle l \,|\, \langle i \,|\, V \,|\, i\rangle \,|\, l\rangle - \langle l \,|\, \langle i \,|\, V \,|\, l\rangle \,|\, i\rangle\} \\ &= \langle l \,|\, U \,|\, l\rangle + \sum_i \{2\,J_{il} - K_{il}\},\end{aligned} \tag{40}$$

where the sum over i as always should be over all MO's, which are filled in the ground state, including $i = l$. (40) is also valid for the eigenvalues ε corresponding to empty MO's, in which case i of course must be different from l. Therefore,

$$\begin{aligned}{}^1E_{lm} &= E_0 - \varepsilon_l + (\varepsilon_m - 2\,J_{lm} + K_{lm}) + J_{lm} + K_{lm} \\ &= E_0 - \varepsilon_l + \varepsilon_m - J_{lm} + 2K_{lm}.\end{aligned} \tag{41}$$

The probability for a transition between the ground state E_0 and the excited state E_{lm} is proportional to the square of the modulus of

$$\mathbf{R} = \int \Psi_0^* \sum_t \mathbf{r}_t \Psi_{lm}\, d\tau. \tag{42}$$

Because of the orthogonality of Ψ_0 and Ψ_{lm} only one term is left in (42), and the terms corresponding to the second sum of (22) vanish,

$$\mathbf{R} = \int \varphi_l^* \mathbf{r}\, \varphi_m\, d\tau = \sum_{q,s} \langle l \,|\, q\rangle \langle q \,|\, \mathbf{r} \,|\, s\rangle \langle s \,|\, m\rangle. \tag{43}$$

According to Mulliken and Rieke [14] the oscillator strength f is

$$f = 1.085 \times 10^{11} \nu a_0^2 \mathbf{R}^* \mathbf{R} = 3.039 \times 10^{-6} \nu \mathbf{R}^* \mathbf{R}, \tag{44}$$

where ν is the wave number in cm^{-1} and $\mathbf{R}$ is measured in a.u.

For the discussion of the wave functions (7), (8) and (9) it is also of interest to calculate the energy of the doubly excited states, where both the electrons from φ_l are promoted to φ_m. As the ionization energy of the second electron in φ_l is $= \varepsilon_l - J_{ll}$, we have

$$E_{mm} = E_0 - (2\varepsilon_l - J_{ll}) + 2(\varepsilon_m - 2J_{lm} + K_{lm}) + J_{mm}$$
$$= E_0 - 2\varepsilon_l + 2\varepsilon_m + J_{ll} + J_{mm} - 4J_{lm} + 2K_{lm}. \tag{45}$$

Energy values computed from (45) will be compared with values obtained by calculation of the best LCAO MO's corresponding to the electron configurations (7)–(9).

C. Discussion of the results for ozone

C1. *Observables in the ground state*

To settle the question which of the configurations (6)–(9) gives the best description of the ground state of ozone, the best LCAO MO's of the $2p$-approximation were determined for each configuration as described in Section B4. The molecular energy E was computed from (25). A comparison between the E-values of the four configurations is given in the first columns of Table 3. It is seen that Ψ_1 yields the lowest energy, but that the other values are quite close to E_1. It can therefore be expected that a superposition of the configurations should improve the energy value significantly. To investigate the order of magnitude of such a treatment a superposition of the configurations (6) and (7) has been studied in the $2p\bar{\pi}$-approximation:

$$\Psi = C_1\Psi_1 + C_2\Psi_2.$$

Ψ_3 and Ψ_4 could not be included as they have different configurations of the $\bar{\sigma}$-electrons a_1 and b_1. The solution of (27) gave an E-value, which was 4.23 ev lower than E_1, and the corresponding values of the coefficients were: $C_1^2 = 0.70$, $C_2^2 = 0.30$. Nevertheless, the main part of the present investigation has been carried out with the assumption that Ψ_1 alone gives an adequate description of the ground state of ozone.

To verify that Ψ_1 is superior to the other functions in the $2s$,$2p$-approximation as well, a few cycles of the variation procedure were carried out for each of the four configurations. Although consistency was not attained, the calculations showed that E_1 is well below the other energy values in this as well as in the other two approximations.

Table 3. Energy $E_m = \int \Psi_m^* H \Psi_m d\tau$ in ev; Ψ_m is obtained from configurations (7), (8) or (9).

	$E_m - E_1$ computed from				
	minimizing of E_m		equation (45)		
	$2p$-appr.	$2p\bar{\pi}$-appr.	$2s$,$2p$-appr.	$2p$-appr.	$2p\bar{\pi}$-appr.
$E_2 - E_1$	8.29	5.80	11.00	21.45	5.80
$E_3 - E_1$	4.28	—	8.02	12.86	—
$E_4 - E_1$	3.52	—	4.10	10.09	—

Table 4. Vertical ionization potentials, $-\varepsilon$ of (14), in ev ($2p$-approximation).

MO of removed electron	$-\varepsilon$ calculated by variation of the MO's in				Max. diff. between ε's
	Ψ_1	Ψ_2	Ψ_3	Ψ_4	
$2b_2$	—	8.7	11.8	13.3	4.6
$3b_1$	14.4	15.3	—	14.5	0.9
$4a_1$	17.3	16.0	15.5	—	1.8
$1a_2$	15.3	—	17.2	17.4	2.1
$1b_2$	19.0	19.2	20.3	21.3	2.3
$3a_1$	28.0	26.0	24.8	26.2	3.2
$2b_1$	31.0	31.7	30.4	30.0	1.7

The energies E_2, E_3 and E_4 have also been computed from (45), using the best LCAO MO's of Ψ_1. These values are listed in the last three columns of Table 3. They differ considerably from the more accurate values of the two preceding columns. Of course, it could not be expected that such a computation should give any E-value lower than E_1. It is, however, interesting to note that the differences $E_m - E_1$, computed in the two different ways, are about proportional to each other in the $2p$-approximation. Furthermore, both ways of computation give $E_2 > E_3 > E_4$ in the $2s,2p$- as well as in the $2p$-approximation.

It is illuminant to consider some details of the results from the variations of Ψ_1, Ψ_2, Ψ_3 and Ψ_4. Table 4 shows the vertical ionization potentials, i.e. minus the orbital energies ε of (14). The last column shows that the differences between corresponding ε-values are of the same magnitude for low and high orbitals. The order of the ε-values is the same in all cases with one exception, i.e. the reversion of the order of the orbital energies of $1a_2$ and $4a_1$ for Ψ_3 and Ψ_1.

It is especially interesting to compare Ψ_1 and Ψ_2, since they have the same kind of a_1 and b_1 orbitals, which are seen to be the $\bar{\sigma}$-orbitals. (As the notations σ and π are used in the sense of Fig. 2 in the present paper, the notations $\bar{\sigma}$ and $\bar{\pi}$ are used in the same way as the usual σ and π symbols of conjugated molecules.) The difference in orbital energies for Ψ_1 and Ψ_2 is never more than 2 ev. Other characteristics of the orbitals are, however, more different. Table 5 reproduces the gross atomic populations $N(r)$ of (34) and the overlap populations $n(i)$ of (37) of the $\bar{\sigma}$- and the $\bar{\pi}$-orbitals of the two configurations. It is seen that the change in the distribution of the $\bar{\pi}$-electrons from $N(\bar{\pi}_a) = 2.00$ in Ψ_2 to $N(\bar{\pi}_a) = 0.62$ in Ψ_1 is accompanied by an equally large change in the opposite direction of the $\bar{\sigma}$-electron distribution from $\Sigma N(\bar{\sigma}_a) = 1.98$ in Ψ_2 to $\Sigma N(\bar{\sigma}_a) = 3.42$ in Ψ_1.

The overlap populations are also quite different. Adopting the assumption that $n(i)$ is a measure of the bond strength [7] one finds from Table 5 that the $\bar{\sigma}$-bonds are considerably stronger in Ψ_2 than in Ψ_1, $3b_1$ being less antibonding in Ψ_2 and $4a_1$ being bonding in Ψ_2 but slightly antibonding in Ψ_1. On the other hand, the strengths of the $\bar{\pi}$-bonds, represented in Table 5 by $\Sigma n(b_2)$ and $n(1a_2)$, are reversed compared to the strengths of the $\bar{\sigma}$-bonds, since the sum of the $\bar{\pi}$-orbitals is seen to be antibonding in Ψ_2 and bonding in Ψ_1. If these results are applicable to unsaturated molecules in general, they indicate that the $\bar{\pi}$-electron approximation should give satisfactory results with reference to energy values including spectral lines (see also Table 12), but

Table 5. Gross atomic populations $N(r)$ of (34) and molecular orbital overlap populations $n(i)$ of (37) for $\bar{\sigma}$- and $\bar{\pi}$-orbitals from Ψ_1 and Ψ_2 ($2p$-approximation).

$\bar{\sigma}$-orbitals					
$N(r)$	Ψ_1	Ψ_2	$n(i)$	Ψ_1	Ψ_2
$N(z_1)$	0.524	1.348	$n(3a_1)$	+0.208	+0.202
$N(y_1)$	1.764	1.663	$n(4a_1)$	−0.034	+0.103
$\Sigma N(\bar{\sigma}_1)$	2.288	3.011	$\Sigma n(a_1)$	+0.175	+0.305
$N(z_a)$	1.702	0.649	$n(2b_1)$	+0.208	+0.230
$N(y_a)$	1.722	1.328	$n(3b_1)$	−0.320	−0.138
$\Sigma N(\bar{\sigma}_a)$	3.424	1.978	$\Sigma n(b_1)$	−0.112	+0.092
$\bar{\pi}$-orbitals					
$N(\bar{\pi}_1)$	1.693	1.000	$n(1b_2)$	+0.218	+0.166
			$n(2b_2)$	—	−0.303
$N(\bar{\pi}_a)$	0.615	2.000	$\Sigma n(b_2)$	+0.218	−0.137
			$n(1a_2)$	−0.036	—

that the bond strengths and dipole moment calculated from the electron distribution of this approximation could give an incorrect picture of the molecule.

In the following, the results of the calculations by use of Ψ_1 of (6) are reported and discussed. The values of energies and dipole moment computed in different approximations are reproduced in Table 6. Here, $E_{\text{diss}} = 3E_{\text{atom}} - E_{\text{mol}}$, where E_{mol} is computed from (25) and $E_{\text{atom}} = 426.69$ ev is the energy of the valence shell of the oxygen atom, computed from the SCF AO's of [12]. The experimental value of E_{mol} has been obtained from the experimental dissociation energy and the spectroscopical value of $E_{\text{atom}} = 433.04$ ev. It should be noted that the computed value of the dissociation energy E_{diss} is much larger in the $2p$-approximation than in the $2s,2p$-approximation. This discrepancy demonstrates clearly the importance of the forced hybridization, discussed by Mulliken [15]. Such a hybridization between the $1s$-shell and the valence orbitals has been computed for LiH by the author [16] and for N_2 by Scherr [17]. The comparatively good agreement between the experimental value and the value of E_{diss} in the $2s,2p$-approximation will possibly disappear in a more complete treatment including $1s$-orbitals, although in this case the effect of the forced hybridization will of course be much smaller than in the case when the interaction of $2s$-orbitals and $2p$-orbitals is neglected, as in the $2p$-approximation.

The dipole moments computed in the different approximations are of the same magnitude as the experimental value, but the sign is reversed in the $2p$-approximation compared to the $2s,2p$- and the $2p\bar{\pi}$-approximations. The latter are supposed to have the correct sign, as it is in accordance with the sign to be expected from the structure formulae I of Fig. 1. The fact that the μ-value of the $2p\bar{\pi}$-approximation is several times larger than the value of the $2s,2p$-approximation is seen to be consistent with the previous discussion of Table 5.

Table 6. Observables of the ground state of ozone: E_{mol} of (25), $E_{\text{diss}} = 3\,E_{\text{atom}} - E_{\text{mol}}$, μ of (22) and ε of (14).

Observable	Experimental value	Values calculated from Ψ_1 in		
		$2s,2p$-appr.	$2p$-appr.	$2p\bar{\pi}$-appr.
E_{mol} (ev)	-1305.32	-1285.13	-1314.01	-86.99
E_{diss} (ev)	$+6.20$	$+5.05$	$+33.94$	$+40.31$
μ (Debye)	$0.58(O_a^+ ?)$	$0.25(O_a^+)$	$1.06(O_a^-)$	$1.26(O_a^+)$
ε (ev) for				
$1a_1$		-47.32	-46.56	—
$1b_1$		-40.96	-39.23	—
$2a_1$		-32.63	-32.98	—
$2b_1$		-25.21	-31.05	—
$3a_1$		-22.81	-27.99	—
$1b_2$		-21.26	-19.02	-22.24
$3b_1$		-15.61	-14.41	—
$4a_1$		-14.82	-17.29	—
$1a_2$		-13.66	-15.26	-11.65
$2b_2$		$-\ 2.00$	$-\ 0.02$	$-\ 2.24$
$5a_1$		$+\ 4.31$	$-\ 0.94$	—
$4b_1$		$+17.12$	$+\ 1.65$	—

The orbital energies ε have in most cases about the same value in the different approximations, the only exception being the ε-values of $2b_1$ and $3a_1$. The agreement between the $2s,2p$- and the $2p\bar{\pi}$-approximations is especially interesting in view of the previous discussion.

It should, however, be noted that the order of the outermost orbital energies is different in the $2p$- and the $2s,2p$-approximations. As no values of experimental ionization energies have been published, it is difficult to tell, which order is the correct one. Furthermore, the order could be changed once more, when interaction with the $1s$-electrons is considered. In fact, for N_2 [17] this interaction increased the computed separation of the $3\sigma_g$ and the $1\pi_u$ orbitals by 0.8 ev. The separation of the orbitals of ozone is of this magnitude: $\Delta\varepsilon(4a_1 - 3b_1) = 0.8$ ev and $\Delta\varepsilon(1a_2 - 4a_1) = 1.1$ ev. In addition, several integrals are computed by rather approximate methods, cf. Section D4. This lack of accuracy may have different effects on the different symmetry species. Judging from the computed ε-values it is therefore impossible to give preference to any of the configurations (3) or (4).

C2. *The molecular orbitals in the ground state*

In Table 7 and Table 8 the self-consistent coefficients $\langle\mu|i\rangle$ of (13) for the LCAO MO's are compiled. The coefficients are given for the two representations discussed in Section B1. When the computed orbitals are to be compared with the configurations (3) and (4), representation (2) should be used. As could be expected, none of the orbitals a_1 or b_1 can be uniquely correlated to any orbital of a linear molecule, i.e. they are not exclusively σ-orbitals or π-orbitals. However, most of them are essen-

Table 7. LCAO coefficients $\langle \mu | i \rangle$ of (13) for the molecular orbitals a_1 and b_1.

MO	2s,2p-approximation					2p-approximation				
	Representation (1)									
	s_1+s_2	s_a	z_1+z_2	z_a	y_1-y_2	s_1+s_2	s_a	z_1+z_2	z_a	y_1-y_2
$1a_1$	+0.319	+0.738	−0.058	+0.144	−0.131	+0.385	+0.790	—	—	—
$2a_1$	+0.971	−0.685	+0.036	+0.118	+0.018	+1.008	−0.735	—	—	—
$3a_1$	−0.382	−0.096	+0.196	+0.802	−0.359	—	—	+0.264	−0.451	+0.761
$4a_1$	+0.078	+0.166	+0.958	−0.467	−0.232	—	—	+0.529	+0.777	+0.421
$5a_1$	−0.313	+0.733	+0.362	+0.551	+1.078	—	—	+0.819	−0.534	−0.563
	s_1-s_2		z_1-z_2	y_a	y_1+y_2	s_1-s_2		z_1-z_2	y_a	y_1+y_2
$1b_1$	+0.738		−0.178	+0.359	−0.145	+1.000		—	—	—
$2b_1$	+0.687		+0.563	−0.562	+0.120	—		−0.263	+0.783	−0.309
$3b_1$	+0.052		−0.433	−0.033	+0.893	—		−0.050	+0.486	+0.980
$4b_1$	−0.565		+0.763	+1.037	+0.530	—		+1.009	+0.545	+0.038
	Representation (2)									
	σ_g			π_u		σ_g			π_u	
	s_1+s_2	$\sigma_1+\sigma_2$	$\sigma_{a1}+\sigma_{a2}$	$\pi_1+\pi_2$	π_a	s_1+s_2	$\sigma_1+\sigma_2$	$\sigma_{a1}+\sigma_{a2}$	$\pi_1+\pi_2$	(s_a)
$1a_1$	+0.319	+0.143	+0.685	−0.011	+0.309	+0.385	—	—	—	+0.790
$2a_1$	+0.971	−0.034	−0.491	−0.024	−0.492	+1.008	—	—	—	−0.735
$3a_1$	+0.382	−0.214	−0.385	+0.342	+0.710	—	+0.792	+0.451	−0.126	—
$4a_1$	−0.078	+0.276	+0.134	+0.955	−0.477	—	−0.629	+0.777	−0.268	—
$5a_1$	+0.313	+1.116	−0.916	−0.188	+0.027	—	−0.081	+0.534	+0.988	—
	σ_u			π_g		σ_u			π_g	
	s_1-s_2	$\sigma_1-\sigma_2$	$\sigma_{a1}-\sigma_{a2}$	$\pi_1-\pi_2$		s_1-s_2	$\sigma_1-\sigma_2$	$\sigma_{a1}-\sigma_{a2}$	$\pi_1-\pi_2$	
$1b_1$	+0.738	+0.212	+0.359	+0.082		+1.000	—	—	—	
$2b_1$	+0.687	−0.371	−0.562	−0.428		—	+0.369	+0.783	+0.074	
$3b_1$	+0.052	−0.586	−0.033	+0.822		—	+0.843	−0.486	−0.533	
$4b_1$	−0.565	−0.827	+1.037	−0.396		—	+0.507	−0.545	+0.855	

Table 8. LCAO coefficients $\langle \mu | i \rangle$ of (13) for the molecular orbitals a_2 and b_2.

MO	2s,2p-approximation		2p-approximation		$2p\bar{\pi}$-approximation	
	$\bar{\pi}_g$		$\bar{\pi}_g$		$\bar{\pi}_g$	
	x_1-x_2		x_1-x_2		x_1-x_2	
$1a_2$	+1.000		+1.000		+1.000	
	$\bar{\pi}_u$		$\bar{\pi}_u$		$\bar{\pi}_u$	
	x_1+x_2	x_a	x_1+x_2	x_a	x_1+x_2	x_a
$1b_2$	+0.539	+0.704	+0.770	+0.456	+0.359	+0.837
$2b_2$	+0.893	−0.768	−0.702	+0.937	+0.978	−0.621

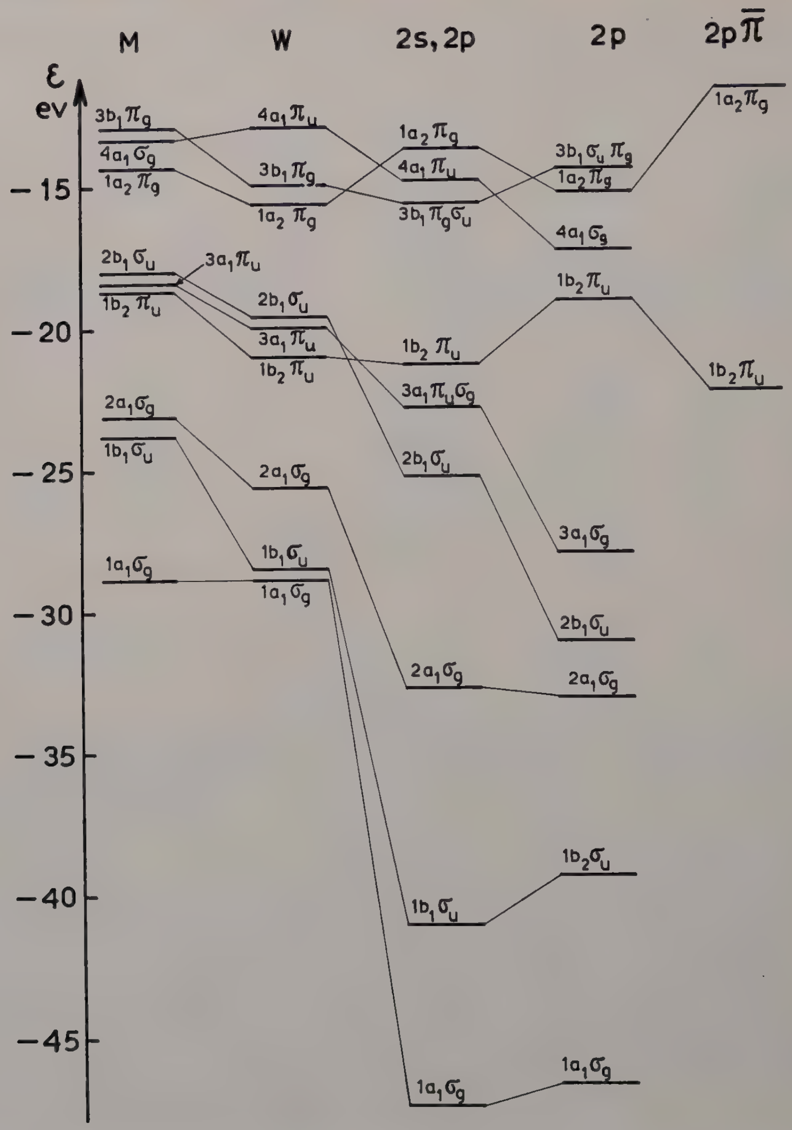

Fig. 3. Energies ε and other characteristics of the MO's of ozone according to Mulliken [1], *M*, Walsh [2], *W*, and different approximations of the present investigation $2s$,$2p$, $2p$ and $2p\bar{\pi}$.

tially σ- or π-orbitals. In Fig. 3 such assignments have been made. In a few cases the σ-part and the π-part of the orbitals are about equally large. Then both symbols have been given with the dominating one in the first place.

In Fig. 3 are also reproduced the orbital energies and characteristics given by Mulliken [1] and Walsh [2]. Mulliken's values are taken from his general orbital scheme. Walsh has not given any energy scale on his scheme. The arbitrary assumption has therefore been made that the lowest and the highest filled orbitals of [2] have the same energies as those of [1] and the intermediate ε-values have been determined by assuming a linear energy scale of the figure in [2]. It should be noted that according to the authors the orbital schemes of [1] and [2] are not supposed to be quantitatively correct. They are, however, reproduced in Fig. 3 in order to show the arrangement of the levels.

Table 7 and Fig. 3 show that the π-parts of the filled a_1 and b_1 orbitals are more dominant according to the $2s$,$2p$-approximation than according to the $2p$-approximation. It is supposed that the π-part will be the most important one also in a more accurate treatment. Consequently, the $4a_1$ MO should be essentially π_u as suggested by Walsh [2]. According to the present computations the level $1b_2$ should lie above the levels $3a_1$ and $2b_1$. It is believed that this result is correct, at least when the d-orbitals of the apex atom do not contribute essentially to $1b_2$. According to my opinion all the s-orbitals of a 90° molecule, $1a_1 = s_1 + s_2$, $2a_1 = s_a$ and $1b_1 = s_1 - s_2$, should have lower energy than any other valence shell orbitals. This point is supported by the fact that in the free oxygen atom the energy of the $2s$-orbital is 33.7 ev whereas that of the $2p$-orbital is only 17.2 ev. Moreover, the bonding $p\bar{\sigma}$-orbitals $3a_1$ and $2b_1$ should be lower than the bonding $p\bar{\pi}$-orbital. Although the spacing of the orbitals is likely to be different in the 120° molecule, I believe that they should have the same order as in the 90° molecule, which is in agreement with both approximations of the present computations.

C3. *Population analysis of the ground state*

The overlap populations $n(i; k, m)$ of (38) and $n(i)$ of (37) for the molecular orbitals are collected in Table 9. The assumption of a qualitative correlation between the overlap population and the bonding power [7] will be adopted in order to discuss the results and compare them with the qualitative description of the orbitals given by Walsh [2]. According to this author the $1a_1$ and $1b_1$ orbitals should be essentially nonbonding lone pairs $s_1 + s_2$ and $s_1 - s_2$. According to the $2s$,$2p$-approximation in the Tables 7 and 9 they could be better described as strong $\bar{\sigma}$-bonds formed by s,p-hybrids at both O_1, O_2 and O_a with $1a_1$ centered on O_a and $1b_1$ on the other atoms. Because of the large overlap of the $2s$-orbitals with the AO's of neighbouring atoms it does not seem to be appropriate to consider the s-electrons as lone pairs, although Table 11 shows that the gross atomic populations of s_1 and s_2 are close to 2.0. The bonding properties expected by Walsh for $2a_1$ and $2b_1$ have not been found for these orbitals but seem to be more characteristic of the lower orbitals. The next higher orbitals of the same species, $3a_1$ and $3b_1$, are slightly O_1–O_a bonding. However, $3b_1$ is essentially localized to the pair O_1, O_2 and shows many similarities with $1a_2$, which could be expected from the general orbital schemes of [1] and [2]. For symmetry reasons the a_2 and b_2 orbitals cannot be complicated by s,p-hybridization as the a_1 and b_1 orbitals and need no comment.

The values of the $2p$-approximation differ considerably from those of the $2s$,$2p$-approximation. However, in both approximations the bonding properties are given by the following scheme:

	Σa_1	Σb_1	a_2	b_2
O_1–O_2	bonding	antibonding	antibonding	bonding
O_1–O_a	antibonding	bonding	nonbonding	bonding

Table 9. Overlap populations $n(i;\,k,\,m)$ of (38) and $n(i)$ of (37) for molecular orbitals and total overlap population n of (39).

MO	2s,2p-approximation			2p-approximation		
	$n(i;\,O_1,\,O_2)$	$n(i;\,O_1,\,O_a)$	$n(i)$	$n(i;\,O_1,\,O_2)$	$n(i;\,O_1,\,O_a)$	$n(i)$
$1a_1$	+0.0120	+0.1530	+0.3180	+0.0054	+0.1141	+0.2337
$2a_1$	+0.0319	−0.2118	−0.3916	+0.0372	−0.2786	−0.5199
$3a_1$	−0.0014	+0.0276	+0.0537	+0.0611	+0.0736	+0.2083
$4a_1$	+0.0391	−0.1131	−0.1871	+0.0273	−0.0305	−0.0337
$(5a_1)$	(+0.1780)	(−0.6425)	(−1.1070)	(+0.0546)	(−0.1364)	(−0.2182)
Σa_1	*+0.082*	*−0.144*	*−0.207*	*+0.131*	*−0.121*	*−0.112*
$1b_1$	−0.0445	+0.1467	+0.2489	−0.0395	—	−0.0395
$2b_1$	−0.0170	−0.0672	−0.1514	−0.0146	+0.1112	+0.2078
$3b_1$	+0.0999	+0.0018	−0.0964	−0.1223	−0.0987	−0.3196
$(4b_1)$	(−0.1230)	(−0.6023)	(−1.3276)	(−0.0366)	(−0.1583)	(−0.3531)
Σb_1	*−0.161*	*+0.081*	*+0.001*	*−0.176*	*+0.013*	*−0.151*
$1b_2$	+0.0097	+0.1071	+0.2238	+0.0198	+0.0992	+0.2182
$(2b_2)$	(+0.0266)	(−0.1936)	(−0.3607)	(+0.0165)	(−0.1858)	(−0.3551)
Σb_2	*+0.010*	*+0.107*	*+0.224*	*+0.020*	*+0.099*	*+0.218*
$1a_2$	−0.0358	—	−0.0358	−0.0358	—	−0.0358
Σa_2	*−0.036*	—	*−0.036*	*−0.036*	—	*−0.036*
$\Sigma i = \Sigma a + \Sigma b$	*−0.106*	*+0.044*	$n =$ *−0.018*	*−0.061*	*−0.010*	$n =$ *−0.081*

	$2p\bar{\pi}$-approximation		
$1b_2$	+0.0043	+0.0849	+0.1741
$(2b_2)$	(+0.0320)	(−0.3430)	(−0.3110)
Σb_2	*+0.004*	*+0.085*	*+0.174*
$1a_2$	−0.0358	—	−0.0358
Σa_2	*−0.036*	—	*−0.036*
$\Sigma i = \Sigma a + \Sigma b$	*−0.032*	*+0.085*	$n =$ *+0.138*

This indicates that there should be a $b_1\bar{\sigma}$-bond and a $b_2\bar{\pi}$-bond between the apex atom and each of the other atoms. According to Table 9 both bonds are weaker than ordinary $\bar{\sigma}$- or $\bar{\pi}$-bonds, where $n(O_1, O_a)$ is computed to be $+0.2$. It is remarkable that the total overlap population n is slightly negative except in the $2p\bar{\pi}$-approximation, and that the total overlap of the s-orbitals in the $2p$-approximation is -0.33. It seems as if the antibonding orbitals were somewhat favoured, when the bonding properties are estimated by population analysis. It is, however, believed that the qualitative picture of the bonding properties, given by Table 9, is correct.

Table 10 shows the overlap populations $n(r, t)$ of (33) between atomic orbitals of representation (2). It is seen that in the $2s,2p$-approximation there is a strong repulsion between s_1 and the orbitals of O_a, especially σ_{a1}. The large overlap integral $\langle s_1|S|\sigma_{a1}\rangle = 0.44$ and the almost complete gross atomic population of s_1, $N(s_1) = 1.97$, give the explanation of this repulsion. Moreover, the strongest a_1 and b_1 bonding is between σ_1 and σ_{a1}. From the point of view of overlap populations it is therefore justified to neglect the s,p-hybridization of the bonding orbitals at the atoms O_1 and O_2, since σ_1 is a pure p-orbital (cf. Table 2).

Table 10. Overlap populations $n(r, t)$ of (33) between atomic orbitals of representation (2) and $n(k, m)$ of (39) between atoms k and m.

$n(r, t)$ or $n(k, m)$	$2s,2p$-approximation			$2p$-approximation		
	Σa_1	Σb_1	$\Sigma i = \Sigma a_1 + \Sigma b_1$	Σa_1	Σb_1	$\Sigma i = \Sigma a_1 + \Sigma b_1$
$n(s_1, s_2)$	+0.0438	−0.0402	+0.0035	+0.0426	−0.0395	+0.0031
$n(s_1, \sigma_2)$	−0.0061	+0.0101	+0.0039	—	—	—
$n(s_1, \pi_2)$	−0.0011	−0.0080	−0.0091	—	—	—
$n(\sigma_1, s_2)$	−0.0061	+0.0101	+0.0039	—	—	—
$n(\sigma_1, \sigma_2)$	+0.0124	−0.0549	−0.0425	+0.0883	−0.0906	−0.0023
$n(\sigma_1, \pi_2)$	−0.0059	−0.0110	−0.0168	−0.0021	−0.0151	−0.0172
$n(\pi_1, s_2)$	−0.0011	−0.0080	−0.0091	—	—	—
$n(\pi_1, \sigma_2)$	−0.0059	−0.0110	−0.0168	−0.0021	−0.0151	−0.0172
$n(\pi_1, \pi_2)$	+0.0517	−0.0483	+0.0034	+0.0044	−0.0162	−0.0118
$n(O_1, O_2)$	*+0.082*	*−0.161*		*+0.131*	*−0.176*	
	Σa_2	Σb_2	$\Sigma i = \Sigma a_2 + \Sigma b_2$	Σa_2	Σb_2	$\Sigma i = \Sigma a_2 + \Sigma b_2$
$n(\bar{\pi}_1, \bar{\pi}_2)$	−0.0358	+0.0097	−0.0261	−0.0358	+0.0198	−0.0160
$n(O_1, O_2)$	*−0.036*	*+0.010*		*−0.036*	*+0.020*	
	Σa_1	Σb_1	$\Sigma i = \Sigma a_1 + \Sigma b_1$	Σa_1	Σb_1	$\Sigma i = \Sigma a_1 + \Sigma b_1$
$n(s_1, \sigma_{a1})$	−0.1804	−0.0552	−0.2357	—	—	—
$n(s_1, \sigma_{a2})$	−0.0035	+0.0011	−0.0025	—	—	—
$n(s_1, \pi_a)$	−0.0017	—	−0.0017	−0.1644	—	−0.1644
$n(\sigma_1, \sigma_{a1})$	+0.0918	+0.1310	+0.2228	−0.0307	−0.0254	−0.0561
$n(\sigma_1, \sigma_{a2})$	+0.0212	−0.0303	−0.0091	+0.0088	−0.0073	+0.0015
$n(\sigma_1, \pi_a)$	−0.0306	—	−0.0306	—	—	—
$n(\pi_1, \sigma_{a1})$	−0.0000	−0.0008	−0.0008	+0.0145	−0.0182	−0.0037
$n(\pi_1, \sigma_{a2})$	−0.0001	+0.0354	+0.0353	+0.0504	+0.0634	+0.1139
$n(\pi_1, \pi_a)$	−0.0408	—	−0.0408	—	—	—
$n(O_1, O_a)$	*−0.144*	*+0.081*		*−0.121*	*+0.013*	
	Σa_2	Σb_2	$\Sigma i = \Sigma a_2 + \Sigma b_2$	Σa_2	Σb_2	$\Sigma i = \Sigma a_2 + \Sigma b_2$
$n(\bar{\pi}_1, \bar{\pi}_a)$	—	+0.1071	+0.1071	—	+0.0992	+0.0992
$n(O_1, O_a)$	—	*+0.107*		—	*+0.099*	

In the $2s,2p$-approximation a smaller contribution to the bonding is given by the interaction of π_1 and σ_{a2}. In the $2p$-approximation, however, this interaction gives the essential part of the bonding, since σ_1 and σ_{a1} are antibonding, which is consistent with the large $N(r)$ values of these orbitals (Table 11). The large σ-populations in the $2p$-approximation can be understood from the fact that the neglected repulsions

Table 11. Gross atomic populations $N(r)$ of (34), $N(k)$ of (35) and charges $Q(r)$ and $Q(k)$ of (36).

	AO or atom	$2s,2p$-approximation				$2p$-approximation			
		$N(r)$ or $N(k)$			$Q(r)$ or $Q(k)$	$N(r)$ or $N(k)$			$Q(r)$ or $Q(k)$
		Σa	Σb	Σi		Σa	Σb	Σi	
Representation (1)	s_1	1.003	0.967	1.969	+0.031	1.000	1.000	2.000	0.000
	z_1	0.905	0.639	1.544	+0.222	0.388	0.136	0.524	+1.242
	y_1	0.290	0.868	1.158	+0.077	0.761	1.003	1.764	−0.530
	x_1	1.000	0.397	1.397	−0.397	1.000	0.693	1.693	−0.693
	s_a	1.874	—	1.874	+0.126	2.000	—	2.000	0.000
	z_a	1.730	—	1.730	−0.730	1.702	—	1.702	−0.702
	y_a	—	1.054	1.054	−0.054	—	1.722	1.722	−0.722
	x_a	—	1.206	1.206	+0.794	—	0.615	0.615	+1.385
Representation (2)	s_1	1.003	0.967	1.969	+0.031	1.000	1.000	2.000	0.000
	σ_1	0.214	0.626	0.840	+0.160	0.998	0.820	1.818	−0.818
	π_1	0.981	0.881	1.862	+0.138	0.151	0.320	0.470	+1.530
	$\bar{\pi}_1$	1.000	0.397	1.397	−0.397	1.000	0.693	1.693	−0.693
	π_a	1.870	—	1.870	−0.537	2.000	—	2.000	0.000
	σ_{a1}	0.867	0.527	1.394	−0.060	0.851	0.861	1.712	−0.712
	σ_{a2}	0.867	0.527	1.394	−0.060	0.851	0.861	1.712	−0.712
	$\bar{\pi}_a$	—	1.206	1.206	+0.794	—	0.615	0.615	+1.385
Repr. (1) or (2)	O$_1$			*6.068*	*−0.068*			*5.981*	*+0.019*
	O$_a$			*5.863*	*+0.137*			*6.039*	*−0.039*
		$2p\bar{\pi}$-approximation							
	x_1	1.000	0.214	1.214	*−0.214*				
	x_a	—	1.572	1.572	*+0.428*				

(σ_1, s_a) and (σ_{a1}, s_1) are very much stronger than the neglected repulsions (π_1, s_a) and (σ_{a2}, s_1), which is seen from the overlap integrals in Table 14. This explains also the result (cf. Fig. 3 and Table 7) that in the $2p$-approximation the a_1 and b_1 orbitals are essentially σ_g and σ_u orbitals respectively.

Table 10 shows also that the negative overlap populations are large compared to the positive ones. So are for instance $n(s_1, \pi_a)$ $(=n(s_1, s_a))$ in the $2p$-approximation and $n(s_1, \sigma_{a1})$ in the $2s,2p$-approximation larger than any of the bonding terms. As mentioned above, the total overlap population is negative, although the computed binding energy is positive. This emphasizes the qualitative character of the results of the population analysis.

Table 11 gives the gross atomic populations $N(r)$ of (34) and $N(k)$ of (35) as well as the charges $Q(r)$ and $Q(k)$ of (36) in e units. Some of the numbers have been discussed above, but a few more points should be mentioned.

Mulliken [7] has pointed out that calculations on both CO and H_2O have given almost the same value, 0.15, for $Q(s_O)$ of the oxygen atom, indicating that this amount of promotion should be characteristic of the oxygen atom in its stable covalent compounds. According to Table 11 $Q(s_1)=0.03$ and $Q(s_a)=0.13$. Both these values are lower than $Q(s_O)$ for CO and H_2O. This can be explained by the facts that the valence state of O_1 is not quite the same as the valence states of most O atoms in stable covalent compounds, and that the set of AO's used in the present investigation is not the same as that used for CO and H_2O. Computations for O_3 carried out by use of such analytical AO's that have been used for CO and H_2O show a much larger amount of promotion than that of Table 11. Consequently, the *importance of the choice of basic AO's must be remembered in the interpretation of the population values.*

With reference to the discussion of Table 5 it should be noted that the $N(x)$ values of Table 11 are quite different in the different approximations, showing the importance of the $\bar{\sigma},\bar{\pi}$-interaction for the details of the electron distribution.

The $Q(r)$ values in the $2p$-approximation, listed in Table 11, are seen to be surprisingly large. All the $\bar{N}(r)$ in $Q(r)$ of (36) are computed from the electron configurations (10) and (11) of the free oxygen atoms. For the $2p$-approximation this is perhaps not justified in view of the fact that $n(\sigma_1, \sigma_{a1})$ of Table 10 is negative, which repulsion is not consistent with the assumtions in (10). If (10) is substituted by the physically less probable configuration

$$O_1\text{: } (2s_1)^2(2p\sigma_1)^2\, 2p\pi_1\, 2p\bar{\pi}_1, \tag{46}$$

giving repulsion between σ_1 and σ_{a1}, we obtain the more reasonable values $Q(\sigma_1) = +0.182$ and $Q(\pi_1) = +0.530$. Nevertheless the remaining $Q(r)$ values are still somewhat *larger* than in the $2s,2p$-approximation in agreement with the larger value of the dipole moment (cf. Table 6). However, the formal charges on the atoms, $Q(O_1)$ and $Q(O_a)$, which of course are independent of the choice of atomic electron configuration, are *smaller* in the $2p$-approximation than in the other approximations. This shows that it is difficult to draw any quantitative conclusions about the dipole moments from the values of the formal charges. The values of the gross atomic populations thus support the impression given by the overlap populations that the *information obtained from the population analysis is qualitatively but not quantitatively correct.*

The results discussed in Sections C1, C2 and C3 show that the neglects, inherent in the $2p$-approximation, are so serious that only the values of the orbital energies (Table 6) can be used with any confidence. When details about orbitals and electron distribution are wanted, the $2p\bar{\pi}$-approximation could be used to obtain some information about the $\bar{\pi}$-orbitals. To obtain information about both $\bar{\sigma}$- and $\bar{\pi}$-orbitals the much more laborious $2s,2p$-approximation must be used.

C4. *Excited states and absorption spectrum*

The experimental investigations of the ozone spectrum have been reviewed by Mulliken [1] and Walsh [2] and are summarized in the first columns of Table 12.

As mentioned in Section B6 an estimate of the energy of the lowest excited states of ozone has been made from (41). The oscillator strength f has been computed from (44), inserting the theoretically computed ν-value. The results are collected in the other columns of Table 12.

Table 12. The absorption spectrum of ozone. f = oscillator strength of (44).

Experimental values			Values computed from						Excited state	Transition from ground state $^1A_1$ of (6)
			2s,2p-appr.		2p-appr.		$2p\bar{\pi}$-appr.			
λ Å	ΔE ev	f	ΔE ev	f	ΔE ev	f	ΔE ev	f		
> 7500	< 1.2	v.w.	1.2	10^{-4}	4.1	10^{-3}	—	—	$^1B_2$	$4a_1 \to 2b_2$
6020 5730	2.06 2.16	10^{-4}	8.2	10^{-3}	7.8	10^{-2}	—	—	$^1A_1$	$4a_1 \to 5a_1$
3525 –	3.5 –	w.	8.4	0.02	15.2	0.02	—	—	$^1B_2$	$3a_1 \to 2b_2$
– 2900	– 4.3		13.5	10^{-3}	6.7	10^{-3}	—	—	$^1B_2$	$1b_2 \to 5a_1$
2550	4.86	0.09	9.1	0.6	9.3	0.3	8.9	0.8	$^1B_1$	$1a_2 \to 2b_2$
			11.7	0.6	5.8	0.2	—	—	$^1B_1$	$3b_1 \to 5a_1$
< 2000	> 6.2		13.8	0.1	12.9	0.1	13.5	0.1	$^1A_1$	$1b_2 \to 2b_2$
			17.6	0.07	16.2	0.09	—	—	$^1A_1$	$3a_1 \to 5a_1$

To estimate the error in the energy values obtained from (41) a comparison can be made with Table 3, where energy values obtained from the analogous equation (45) can be checked against more accurate values. This shows that the energy values of Table 12 may be incorrect by more than 10 ev. Moreover, Table 3 shows a large discrepancy between the different approximations, which is also found in Table 12. The values of ΔE must therefore be considered as very uncertain.

It is, however, interesting to notice that the $\bar{\pi}$–$\bar{\pi}$ transitions $1a_2 \to 2b_2$ and $1b_2 \to 2b_2$ are almost equal in all approximations. It can, therefore, be expected that no drastic change of these transitions will be obtained by a more accurate calculation. In order to verify this, a calculation with superposition of different configurations has been carried out in the $2p\bar{\pi}$-approximation. In this calculation the following configurations have been considered for the ground state:

$$\Psi_0\colon\quad C_1\,(1b_2)^2(1a_2)^2 + C_2\,(2b_2)^2(1a_2)^2 + C_3\,(1b_2)^2(2b_2)^2, \tag{47}$$

and for the excited state $^1B_1$:

$$\Psi_e\colon\quad C_4\,(1b_2)^2\,1a_2\,2b_2 + C_5\,(2b_2)^2\,1a_2\,1b_2. \tag{48}$$

By use of (47) and (48) E_0 is lowered by 4.3 ev and E_e by 3.6 ev, so the difference $E_e - E_0$ is only changed by 0.7 ev.

Other transitions, reproduced in Table 12, where the results of the 2s,2p- and the 2p-approximations are very different, could easily change much more drastically, when superposition of configurations is included. It is, therefore, difficult to correlate the absorption bands with the electron transitions by comparison of experimental and theoretical ΔE-values. The correlation is, however, facilitated by the f-values, which are much more similar in the different approximations than the ΔE-values. The following tentative assignations could therefore be made. The observed, very weak, infrared band could represent the $4a_1 \to 2b_2$ transition and the weak, visible band the $4a_1 \rightarrow 5a_1$ transition. Walsh [2] has suggested that the $4a_1 \rightarrow 2b_2$ transition should give rise to one of these two bands, but he expected the $4a_1 \rightarrow 5a_1$ transition to give a band in the ultraviolet. According to the present results all transitions to $5a_1$ are likely to give bands of longer wave lengths than expected by Walsh. The weak absorption in the near ultraviolet could originate from the $3a_1 \rightarrow 2b_2$ or the $1b_2 \rightarrow 5a_1$ transition but most unprobably from the $1a_2 \rightarrow 2b_2$ transition suggested by Walsh. The last-mentioned transition has a very large f-value in all approximations. Therefore, it could possibly correspond to the strong absorption at 2550 Å, in which the $3b_1 \rightarrow 5a_1$ transition also could be involved. The $1b_2 \rightarrow 2b_2$ and $3a_1 \rightarrow 5a_1$ transitions are likely to belong to the far ultraviolet. Finally, all transitions to $4b_1$ should give rise to absorptions at much shorter wave lengths than any of the transitions listed in Table 12.

D. Appendix: Details of the calculations

D 1. *Calculation of molecular orbital coefficients*

The tedious numerical computations of the present investigation consist partly of the determination of the coefficients of the SCF MO's and partly of the computation of the basic integrals. All the numerical work has been carried out on a desk machine.

The coefficients of the SCF MO's were determined by standard methods. The secular equations (20) of 5th and 4th order were solved by the method of James and Coolidge [19].

Scherr [17] has pointed out that in the case of N_2 the SCF MO's can be found from a few iterations by use of an extrapolation procedure. A similar, labour-saving extrapolation cannot be carried out in the case of O_3. The reason seems to be that a simple relation between the successive changes of the coefficients exists only, when the incompletely filled MO's belong to a single species, as in the case of N_2. In the case of O_3, however, the incompletely filled MO's belong to three different species, which interact in a very intricate way.

D 2. *Notations and parameter values of basic integrals*

In the following some details of the calculations of the basic integrals will be mentioned. All values in the Appendix will be given in atomic units. In these units the O_1–O_a distance is 2.411 ± 0.006 a.u. and the O_1–O_2 distance is 4.12 ± 0.02 a.u. [4, 5]. Since in [12] the radial functions $P(r)$ of the SCF AO's are mostly given at r-intervals of 0.2 a.u., it is hardly possible to compute the integrals for other interatomic distances R than $R = 0.2\ N$ a.u., where N is an integer. In the present investigation the parameters have, therefore, been chosen as follows:

$$R_{1a} = R_{2a} = 2.40 \text{ a.u.}$$

$$R_{12} = 4.20 \text{ a.u.}$$

These R-values correspond to an apex angle of 122°.

As in Section B4, the suffixes k, l and m will be used to distinguish the atoms O_k, $k = 1, 2, a$, and the suffixes t and u to distinguish the different electrons. r_{kt}, for example, is the distance of electron t from atom O_k.

The 1*s* AO's will be denoted K. For the L shell AO's the notations of Section B1 will be used.

D 3. *Classification of integrals*

In this section the different kinds of integrals occurring in the calculations of molecular energy (23) and dipole moments (22), (42) are classified.

The one-electron operator U_t of (23) is the sum of the kinetic energy T_t of the electron t and the potential energy of the electron in the field of the nuclei and the inner electrons:

$$U_t = T_t + \sum_k U_{kt}. \tag{49}$$

The operator U_{kt} of (49) is defined by

$$U_{kt}\,\psi(t) = -\frac{Z_k}{r_{kt}}\,\psi(t) + \\ + \sum_q \{2 \int \chi_q^*(u)\, V_{tu}\, \chi_q(u)\, d\tau_u \cdot \psi(t) - \int \chi_q^*(u)\, V_{tu}\, \psi(u)\, d\tau_u \cdot \chi_q(t)\}. \tag{50}$$

The penetration integral $\langle r | U_{kt} | s \rangle$ is, therefore, a sum of a one-electron, potential field integral, $\langle r | -Z_k r_{kt}^{-1} | s \rangle$, and two-electron integrals of the general type

$$(b\,c\,|\,d\,f) = \int \int \chi_b^*(t)\, \chi_d^*(u)\, V_{tu}\, \chi_c(t)\, \chi_f(u)\, d\tau_t\, d\tau_u. \tag{51}$$

In (50) $Z_k = 8$ in all approximations. The sum over q consists of a single term in the $2s$,$2p$-approximation, i.e. $q = K_k$, and of two terms in the $2p$-approximation, i.e. $q = K_k$ and s_k. In the $2p\bar{\pi}$-approximation the sum is extended over the $p\bar{\sigma}$ AO's as well. There are three $p\bar{\sigma}$ AO's of O_1 or O_2, $(2p\pi_k)^2$, $2p\sigma_k$, and two of O_a, $2p\sigma_{a1}$, $2p\sigma_{a2}$, cf. (10) and (11).

The electron interaction operator $2J_t - K_t$ of (23) and (16) gives rise to two-electron integrals of the general type given in (51).

The dipole moment operators of (22) and (42) give rise to one-electron integrals $\langle b | z_t | c \rangle$, $\langle b | x_t | c \rangle$ and $\langle b | y_t | c \rangle$. For the computation of the total molecular moment the apex atom O_a is chosen as the origin of the common coordinate system. The coordinates of O_1 and O_2 are x_k, y_k, z_k, $k = 1, 2$.

Finally, the lack of orthogonality between the AO's gives rise to one-electron, two-centre overlap integrals $\langle b | S | c \rangle$.

The necessary integrals are thus partly one-electron and partly two-electron integrals. Furthermore, they can be classified as one-centre, two-centre and three-centre integrals. Only members of the two first-mentioned classes can be computed with an accuracy, corresponding to the accuracy of the SCF functions for oxygen, given by Hartree, Hartree and Swirles [12].

D 4. *Methods of integral computation*

All one-centre integrals have been computed by numerical integration according to Simpson's rule and using the intervals of the radial distance r given in [12].

All one-electron, two-centre integrals and the two-electron, two-centre Coulomb integrals $(b_k c_k | d_m f_m)$ and hybrid integrals $(b_k c_k | d_k f_m)$ have been computed by expanding the AO's in spherical harmonics around one of the centres as described by Lundqvist and Löwdin [20]. The operator r_{tu}^{-1} was expanded in spherical harmonics as usual. After integration over the angular variables most terms in the series disappeared. The final numerical integration over r was carried out by use of intervals of 0.2 a.u. In the ranges, where the intervals given in [12] are larger, the interpolation was carried out by use of a function $\alpha r^n e^{-\beta r}$, where α and β were determined so as to fit the given points.

The two-electron, two-centre exchange integrals $(b_k c_m | d_k f_m)$ as well as the one-electron, three-centre integrals $\langle b_k | -Z_l r_{lt}^{-1} | c_m \rangle$ and the two-electron, three-centre integrals, $(b_k c_k | d_l f_m)$ and $(b_k c_l | d_k f_m)$, were computed by less accurate methods. In all these cases the expansion of the AO's in spherical harmonics according to [20] gives rise to slowly converging, doubly infinite series. These integrals were, therefore, computed as follows.

Each AO was expanded in the eigenfunctions K, s, y, z, x ... of the Hartree-Fock operator of an oxygen atom. The series should of course in principle include all higher AO's, $3s$, $3p$, $3d$ ... as well. As these higher AO's are not known for oxygen, the series was broken off after the L-shell. For the exchange integral $(h_1 h_2 | h_1 h_2)$ of two hydrogen atoms it was shown that the contribution from higher shells is of lower order of magnitude than the first shell contribution. It is reasonable to assume a similar result for the case of oxygen. The break off after the L-shell is, however, somewhat unsatisfactory, and the accuracy of these groups of integrals is not as high as desirable. As there are about six hundred integrals in these groups, it was not possible to carry out any still more time-consuming computation.

The general formula used for the computation of the three-centre integrals $(b_k c_l | d_k f_m)$ is:

$$\begin{aligned}
4\,(b_k c_l | d_k f_m) &= \sum_{q_k} \sum_{r_k} \langle q_k | S | c_l \rangle \langle r_k | S | f_m \rangle (b_k q_k | d_k r_k) + \\
&\quad + \sum_{q_l} \sum_{r_k} \langle b_k | S | q_l \rangle \langle r_k | S | f_m \rangle (q_l c_l | d_k r_k) + \\
&\quad + \sum_{q_k} \sum_{r_m} \langle q_k | S | c_l \rangle \langle d_k | S | r_m \rangle (b_k q_k | r_m f_m) + \\
&\quad + \sum_{q_l} \sum_{r_m} \langle b_k | S | q_l \rangle \langle d_k | S | r_m \rangle (q_l c_l | r_m f_m). \qquad (52)
\end{aligned}$$

Expressions similar to (52) have been used for the other groups of integrals. (52) is a generalization of the formula given by Mulliken [21]. A similar expression has been discussed by Ruedenberg [22].

D 5. *Numerical values of some integrals*

From considerations of space, only integrals over atomic orbitals are listed below, and of these the numerous two-electron, three-centre integrals are omitted. The integrals over symmetry orbitals can be computed from the tables as indicated in

Section B1. Most of the tables give integrals over AO's of representation (1). The reason for this is that it is inconvenient to express the three-centre integrals in the AO's of the less formal representation (2). The self-consistent field computations have, therefore, been carried out in representation (1), and the two-centre integrals are accordingly given in this representation. Only the overlap integrals are also given in representation (2).

As it can be easily deduced from symmetry, which integrals are equal, or differ only with respect to sign, only one integral of such a group is usually given.

Table 13. Overlap integrals $\langle b|S|c\rangle$ of atomic orbitals of representation (1) in a.u.

$\chi_b\,\chi_c$	$\langle b_1|S|c_2\rangle$	$\chi_b\,\chi_c$	$\langle b_1|S|c_a\rangle$
$s_1\,s_2$	+0.0380	$s_1\,s_a$	+0.2707
$s_1\,y_2$	+0.0828	$s_1\,y_a$	+0.3068
$s_1\,z_2$	0	$s_1\,z_a$	+0.1697
$y_1\,y_2$	−0.1129	$y_1\,y_a$	−0.1477
$y_1\,z_2$	0	$y_1\,z_a$	−0.1941
$z_1\,z_2$	+0.0345	$z_1\,z_a$	+0.0957
$x_1\,x_2$	+0.0345	$x_1\,x_a$	+0.2030

Table 14. Overlap integrals $\langle b|S|c\rangle$ of atomic orbitals of representation (2) in a.u.

$\chi_b\,\chi_c$	$\langle b|S|c\rangle$	
	$2s,2p$-appr.	$2p$-appr.
$s_1\,s_2$	+0.0380	+0.0380
$s_1\,\sigma_2$	+0.0725	+0.0725
$s_1\,\pi_2$	−0.0401	−0.0401
$\sigma_1\,\sigma_2$	+0.0946	+0.0946
$\sigma_1\,\pi_2$	−0.0332	−0.0332
$\pi_1\,\pi_2$	+0.0529	+0.0529
$\bar{\pi}_1\,\bar{\pi}_2$	+0.0345	+0.0345
$s_1\,\sigma_{a1}$	+0.4425	+0.3369
$s_1\,\sigma_{a2}$	+0.0087	−0.0969
$s_1\,\pi_a$	+0.0177	+0.2707
$\sigma_1\,\sigma_{a1}$	+0.4107	+0.2451
$\sigma_1\,\sigma_{a2}$	+0.0950	−0.0705
$\sigma_1\,\pi_a$	+0.1016	+0.3506
$\pi_1\,\sigma_{a1}$	−0.0030	−0.0561
$\pi_1\,\sigma_{a2}$	−0.1420	−0.1951
$\pi_1\,\pi_a$	+0.1450	+0.0000
$\bar{\pi}_1\,\bar{\pi}_a$	+0.2030	+0.2030

Table 15. One-electron potential energy integrals $\langle b|-Z_k r_{t\,k}^{-1}|c\rangle$ of atomic orbitals of representation (1) in a.u.

$\chi_b \chi_c$	$\langle b\|-8/r_{1t}\|c\rangle$	$\langle b\|-8/r_{at}\|c\rangle$	$\langle b\|-8/r_{2t}\|c\rangle$
$s_1 s_1$	−10.1136	−3.3211	−1.9038
$y_1 y_1$	− 8.8874	−3.5503	−1.9682
$z_1 z_1$	− 8.8874	−3.2416	−1.8625
$x_1 x_1$	− 8.8874	−3.1054	−1.8625
$s_1 y_1$	0	+0.7878	+0.3032
$s_1 z_1$	0	+0.4359	0
$y_1 z_1$	0	−0.2462	0
$s_1 s_2$	− 0.1466	−0.1915	−0.1466
$s_1 y_2$	− 0.4365	−0.3440	−0.2456
$s_1 z_2$	0	+0.0260	0
$y_1 y_2$	+ 0.4472	+0.4666	+0.4472
$y_1 z_2$	0	−0.0363	0
$z_1 z_2$	− 0.1115	−0.1119	−0.1115
$x_1 x_2$	− 0.1115	−0.1072	−0.1115
$s_1 s_a$	− 1.4841	−1.4841	−0.6699
$s_1 y_a$	− 2.0182	−1.4376	−0.7306
$s_1 z_a$	− 1.1166	−0.7954	−0.4878
$y_1 s_a$	+ 1.4376	+2.0182	+0.8367
$y_1 y_a$	+ 1.0751	+1.0751	+0.3084
$y_1 z_a$	+ 1.1114	+1.1114	+0.5811
$z_1 s_a$	+ 0.7954	+1.1166	+0.3426
$z_1 y_a$	+ 1.1114	+1.1114	+0.4693
$z_1 z_a$	− 0.3187	−0.3187	−0.2305
$x_1 x_a$	− 0.9336	−0.9336	−0.5043

Table 16. Kinetic energy integrals $\langle b|T|c\rangle$ of atomic orbitals of representation (1) in a.u.

$\chi_b \chi_c$	$\langle b\|T\|c\rangle$	$\chi_b \chi_c$	$\langle b\|T\|c\rangle$
$s_k s_k$	+3.1060	$p_k p_k$	+2.5422
$s_1 s_2$	−0.0163	$s_1 s_a$	+0.0722
$s_1 y_2$	+0.0181	$s_1 y_a$	+0.1195
$s_1 z_2$	0	$s_1 z_a$	+0.0661
$y_1 y_2$	−0.0445	$y_1 y_a$	−0.1925
$y_1 z_2$	0	$y_1 z_a$	−0.1459
$z_1 z_2$	−0.0011	$z_1 z_a$	−0.0096
$x_1 x_2$	−0.0011	$x_1 x_a$	+0.0712

Table 17. One-electron dipole integrals $\langle b|z_t|c\rangle$ of atomic orbitals of representation (1) in a.u.

$z_1 = z_2 = +1.1619$ a.u.

$\chi_b \chi_c$	$\langle b\|z_t\|c\rangle$	$\chi_b \chi_c$	$\langle b\|z_t\|c\rangle$
$\chi_1 \chi_1$	+1.1619	$\chi_a \chi_a$	0
$s_1 z_1$	+0.6693	$s_a z_a$	+0.6693
$s_1 s_2$	+0.0442	$s_1 s_a$	+0.1575
$s_1 y_2$	+0.0962	$s_1 y_a$	+0.1951
$s_1 z_2$	+0.0327	$s_1 z_a$	+0.2954
$y_1 s_2$	−0.0962	$y_1 s_a$	−0.1686
$y_1 y_2$	−0.1312	$y_1 y_a$	−0.0860
$y_1 z_2$	−0.0717	$y_1 z_a$	−0.3269
$z_1 s_2$	+0.0327	$z_1 s_a$	+0.0964
$z_1 y_2$	+0.0717	$z_1 y_a$	+0.1006
$z_1 z_2$	+0.0401	$z_1 z_a$	+0.0555
$x_1 x_2$	+0.0401	$x_1 x_a$	+0.1182

Table 18. One-electron dipole integrals $\langle b|y_t|c\rangle$ of atomic orbitals of representation (1) in a.u.

$y_1 = -y_2 = +2.1000$ a.u.

$\chi_b \chi_c$	$\langle b\|y_t\|c\rangle$
$\chi_1 \chi_1$	+2.1000
$s_1 y_1$	+0.6693
$s_a y_a$	+0.6693
$s_1 y_2$	+0.0669
$s_1 s_a$	+0.2847
$s_1 y_a$	+0.5401
$s_1 z_a$	+0.1951
$y_1 s_a$	−0.1150
$y_1 y_a$	−0.1567
$y_1 z_a$	−0.0868
$z_1 s_a$	−0.1686
$z_1 y_a$	−0.3230
$z_1 z_a$	+0.1002
$x_1 x_a$	+0.2136

Table 19. One-electron dipole integrals $\langle b|x_t|c\rangle$ of atomic orbitals of representation (1) in a.u.

$x_1 = x_2 = 0.$

$\chi_b\,\chi_c$	$\langle b\|x_t\|c\rangle$
$s_k\,x_k$	+0.6693
$s_1\,x_2$	+0.0327
$y_1\,x_2$	−0.0717
$z_1\,x_2$	0
$s_1\,x_a$	+0.1874
$y_1\,x_a$	−0.2135
$z_1\,x_a$	−0.1181

Table 20. Two-electron, one-centre integrals $(b_k c_k|d_k f_k)$ of atomic orbitals of representation (1) in a.u.

$\chi_b\,\chi_c$	$\chi_d\,\chi_f$	$(b_k c_k\|d_k f_k)$
KK	KK	+4.7473
KK	ss	+1.1345
KK	yy	+1.0988
ss	ss	+0.7972
ss	yy	+0.7733
yy	yy	+0.8080
yy	zz	+0.7275
Ks	Ks	+0.0777
Ky	Ky	+0.0351
sy	sy	+0.1572
yz	yz	+0.0403
KK	Ks	−0.4798
Ks	ss	−0.0215
Ks	yy	−0.0151
Ky	sy	+0.0378

Table 21. Two-electron, two-centre, Coulomb integrals $(b_k c_k | d_m f_m)$ of atomic orbitals of representation (1) in a.u.

$\chi_b \chi_c$	$\chi_d \chi_f$	$(b_1 c_1 | d_2 f_2)$	$\chi_b \chi_c$	$\chi_d \chi_f$	$(b_1 c_1 | d_a f_a)$
$K_1 K_1$	$s_2 s_2$	+0.2381	$K_1 K_1$	$s_a s_a$	+0.4159
$K_1 K_1$	$y_2 y_2$	+0.2477	$K_1 K_1$	$y_a y_a$	+0.4435
$K_1 K_1$	$z_2 z_2$	+0.2329	$K_1 K_1$	$z_a z_a$	+0.4052
$K_1 K_1$	$x_2 x_2$	+0.2329	$K_1 K_1$	$x_a x_a$	+0.3883
$K_1 K_1$	$s_2 y_2$	+0.0379	$K_1 K_1$	$s_a y_a$	+0.0981
$K_1 K_1$	$s_2 z_2$	0	$K_1 K_1$	$s_a z_a$	+0.0543
$K_1 K_1$	$y_2 z_2$	0	$K_1 K_1$	$y_a z_a$	+0.0306
$s_1 s_1$	$s_2 s_2$	+0.2412	$s_1 s_1$	$s_a s_a$	+0.4055
$s_1 s_1$	$y_2 y_2$	+0.2471	$s_1 s_1$	$y_a y_a$	+0.4261
$s_1 s_1$	$z_2 z_2$	+0.2327	$s_1 s_1$	$z_a z_a$	+0.3979
$s_1 s_1$	$x_2 x_2$	+0.2327	$s_1 s_1$	$x_a x_a$	+0.3855
$s_1 s_1$	$s_2 y_2$	+0.0377	$s_1 s_1$	$s_a y_a$	+0.0871
$s_1 s_1$	$s_2 z_2$	0	$s_1 s_1$	$s_a z_a$	+0.0482
$s_1 s_1$	$y_2 z_2$	0	$s_1 s_1$	$y_a z_a$	+0.0225
$y_1 y_1$	$y_2 y_2$	+0.2575	$y_1 y_1$	$y_a y_a$	+0.4379
$y_1 y_1$	$z_2 z_2$	+0.2415	$y_1 y_1$	$z_a z_a$	+0.4192
$y_1 y_1$	$x_2 x_2$	+0.2415	$y_1 y_1$	$x_a x_a$	+0.4004
$y_1 y_1$	$s_2 y_2$	+0.0420	$y_1 y_1$	$s_a y_a$	+0.0854
$y_1 y_1$	$s_2 z_2$	0	$y_1 y_1$	$s_a z_a$	+0.0613
$y_1 y_1$	$y_2 z_2$	0	$y_1 y_1$	$y_a z_a$	+0.0265
$z_1 z_1$	$z_2 z_2$	+0.2283	$z_1 z_1$	$z_a z_a$	+0.3840
$z_1 z_1$	$x_2 x_2$	+0.2276	$z_1 z_1$	$x_a x_a$	+0.3758
$z_1 z_1$	$s_2 y_2$	+0.0352	$z_1 z_1$	$s_a y_a$	+0.0877
$z_1 z_1$	$s_2 z_2$	0	$z_1 z_1$	$s_a z_a$	+0.0345
$z_1 z_1$	$y_2 z_2$	0	$z_1 z_1$	$y_a z_a$	+0.0165
$x_1 x_1$	$x_2 x_2$	+0.2283	$x_1 x_1$	$x_a x_a$	+0.3681
$x_1 x_1$	$s_2 y_2$	+0.0352	$x_1 x_1$	$s_a y_a$	+0.0776
$x_1 x_1$	$s_2 z_2$	0	$x_1 x_1$	$s_a z_a$	+0.0429
$x_1 x_1$	$y_2 z_2$	0	$x_1 x_1$	$y_a z_a$	+0.0196
$s_1 y_1$	$s_2 y_2$	−0.0119	$s_1 y_1$	$s_a y_a$	−0.0222
$s_1 y_1$	$s_2 z_2$	0	$s_1 y_1$	$s_a z_a$	−0.0276
$s_1 y_1$	$y_2 z_2$	0	$s_1 y_1$	$y_a z_a$	−0.0113
$s_1 z_1$	$s_2 z_2$	+0.0060	$s_1 z_1$	$s_a z_a$	+0.0124
$s_1 z_1$	$y_2 z_2$	+0.0025	$s_1 z_1$	$y_a z_a$	+0.0025
$y_1 z_1$	$y_2 z_2$	−0.0012	$y_1 z_1$	$y_a z_a$	+0.0007
$s_1 x_1$	$s_2 x_2$	+0.0060	$s_1 x_1$	$s_a x_a$	+0.0277
$s_1 x_1$	$y_2 x_2$	+0.0025	$s_1 x_1$	$y_a x_a$	+0.0127
$s_1 x_1$	$z_2 x_2$	0	$s_1 x_1$	$z_a x_a$	+0.0070
$y_1 x_1$	$y_2 x_2$	−0.0012	$y_1 x_1$	$y_a x_a$	−0.0041
$y_1 x_1$	$z_2 x_2$	0	$y_1 x_1$	$z_a x_a$	−0.0058
$z_1 x_1$	$z_2 x_2$	+0.0007	$z_1 x_1$	$z_a x_a$	+0.0032

Table 22. Two-electron, two-centre, exchange integrals $(b_k c_m | d_k f_m)$ of atomic orbitals of representation (1) in a.u.

$\chi_b \chi_c$	$\chi_d \chi_f$	$(b_1 c_2 \mid d_1 f_2)$	$\chi_b \chi_c$	$\chi_d \chi_f$	$(b_1 c_a \mid d_1 f_a)$
$K_1 s_2$	$K_1 s_2$	+0.0000	$K_1 s_a$	$K_1 s_a$	+0.0006
$K_1 y_2$	$K_1 y_2$	+0.0000	$K_1 y_a$	$K_1 y_a$	+0.0012
$K_1 z_2$	$K_1 z_2$	+0.0000	$K_1 z_a$	$K_1 z_a$	+0.0004
$K_1 x_2$	$K_1 x_2$	+0.0000	$K_1 x_a$	$K_1 x_a$	+0.0001
$K_1 s_2$	$K_1 y_2$	+0.0001	$K_1 s_a$	$K_1 y_a$	−0.0001
$K_1 s_2$	$K_1 z_2$	0	$K_1 s_a$	$K_1 z_a$	−0.0001
$K_1 y_2$	$K_1 z_2$	0	$K_1 y_a$	$K_1 z_a$	+0.0006
$s_1 s_2$	$s_1 s_2$	+0.0014	$s_1 s_a$	$s_1 s_a$	+0.0654
$s_1 y_2$	$s_1 y_2$	+0.0040	$s_1 y_a$	$s_1 y_a$	+0.0739
$s_1 z_2$	$s_1 z_2$	+0.0003	$s_1 z_a$	$s_1 z_a$	+0.0294
$s_1 x_2$	$s_1 x_2$	+0.0003	$s_1 x_a$	$s_1 x_a$	+0.0098
$s_1 s_2$	$s_1 y_2$	+0.0023	$s_1 s_a$	$s_1 y_a$	+0.0667
$s_1 s_2$	$s_1 z_2$	0	$s_1 s_a$	$s_1 z_a$	+0.0369
$s_1 y_2$	$s_1 z_2$	0	$s_1 y_a$	$s_1 z_a$	+0.0355
$y_1 y_2$	$y_1 y_2$	+0.0078	$y_1 y_a$	$y_1 y_a$	+0.0307
$y_1 z_2$	$y_1 z_2$	+0.0008	$y_1 z_a$	$y_1 z_a$	+0.0365
$y_1 x_2$	$y_1 x_2$	+0.0008	$y_1 x_a$	$y_1 x_a$	+0.0097
$y_1 s_2$	$y_1 y_2$	+0.0057	$y_1 s_a$	$y_1 y_a$	+0.0422
$y_1 s_2$	$y_1 z_2$	0	$y_1 s_a$	$y_1 z_a$	+0.0463
$y_1 y_2$	$y_1 z_2$	0	$y_1 y_a$	$y_1 z_a$	+0.0236
$z_1 z_2$	$z_1 z_2$	+0.0006	$z_1 z_a$	$z_1 z_a$	+0.0094
$z_1 x_2$	$z_1 x_2$	+0.0000	$z_1 x_a$	$z_1 x_a$	+0.0036
$z_1 s_2$	$z_1 y_2$	+0.0003	$z_1 s_a$	$z_1 y_a$	+0.0303
$z_1 s_2$	$z_1 z_2$	0	$z_1 s_a$	$z_1 z_a$	−0.0061
$z_1 y_2$	$z_1 z_2$	0	$z_1 y_a$	$z_1 z_a$	−0.0067
$x_1 x_2$	$x_1 x_2$	+0.0006	$x_1 x_a$	$x_1 x_a$	+0.0242
$x_1 s_2$	$x_1 y_2$	+0.0003	$x_1 s_a$	$x_1 y_a$	+0.0068
$x_1 s_2$	$x_1 z_2$	0	$x_1 s_a$	$x_1 z_a$	+0.0038
$x_1 y_2$	$x_1 z_2$	0	$x_1 y_a$	$x_1 z_a$	+0.0048
$s_1 s_2$	$y_1 y_2$	−0.0030	$s_1 s_a$	$y_1 y_a$	−0.0406
$s_1 y_2$	$y_1 s_2$	−0.0041	$s_1 y_a$	$y_1 s_a$	−0.0681
$s_1 s_2$	$y_1 z_2$	0	$s_1 s_a$	$y_1 z_a$	−0.0418
$s_1 z_2$	$y_1 s_2$	0	$s_1 z_a$	$y_1 s_a$	−0.0411
$s_1 y_2$	$y_1 z_2$	0	$s_1 y_a$	$y_1 z_a$	−0.0399
$s_1 z_2$	$y_1 y_2$	0	$s_1 z_a$	$y_1 y_a$	−0.0222
$s_1 s_2$	$z_1 z_2$	+0.0007	$s_1 s_a$	$z_1 z_a$	+0.0118
$s_1 z_2$	$z_1 s_2$	+0.0001	$s_1 z_a$	$z_1 s_a$	−0.0166
$s_1 y_2$	$z_1 z_2$	+0.0014	$s_1 y_a$	$z_1 z_a$	+0.0132
$s_1 z_2$	$z_1 y_2$	+0.0002	$s_1 z_a$	$z_1 y_a$	−0.0276
$y_1 y_2$	$z_1 z_2$	−0.0019	$y_1 y_a$	$z_1 z_a$	−0.0085
$y_1 z_2$	$z_1 y_2$	−0.0001	$y_1 z_a$	$z_1 y_a$	+0.0214
$s_1 s_2$	$x_1 x_2$	+0.0007	$s_1 s_a$	$x_1 x_a$	+0.0350
$s_1 x_2$	$x_1 s_2$	+0.0001	$s_1 x_a$	$x_1 s_a$	+0.0061

Table 22 *(continued)*

$\chi_b\chi_c$	$\chi_d\chi_f$	$(b_1c_2 \mid d_1f_2)$	$\chi_b\chi_c$	$\chi_d\chi_f$	$(b_1c_a \mid d_1f_a)$
s_1y_2	x_1x_2	$+0.0014$	s_1y_a	x_1x_a	$+0.0367$
s_1x_2	x_1y_2	$+0.0002$	s_1x_a	x_1y_a	$+0.0046$
s_1z_2	x_1x_2	0	s_1z_a	x_1x_a	$+0.0203$
s_1x_2	x_1z_2	0	s_1x_a	x_1z_a	$+0.0026$
y_1y_2	x_1x_2	-0.0019	y_1y_a	x_1x_a	-0.0197
y_1x_2	x_1y_2	-0.0001	y_1x_a	x_1y_a	-0.0019
y_1z_2	x_1x_2	0	y_1z_a	x_1x_a	-0.0234
y_1x_2	x_1z_2	0	y_1x_a	x_1z_a	-0.0016
z_1z_2	x_1x_2	$+0.0006$	z_1z_a	x_1x_a	$+0.0096$
z_1x_2	x_1z_2	$+0.0000$	z_1x_a	x_1z_a	$+0.0001$

Table 23. Two electron, two-centre hybrid integrals $(b_kc_k \mid d_kf_m)$ of atomic orbitals of representation (1) in a.u.

$\chi_b\chi_c$	$\chi_d\chi_f$	$(b_1c_1 \mid d_1f_2)$	$\chi_b\chi_c$	$\chi_d\chi_f$	$(b_1c_1 \mid d_1f_a)$
K_1K_1	s_1s_2	$+0.0187$	K_1K_1	s_1s_a	$+0.1949$
K_1K_1	s_1y_2	$+0.0535$	K_1K_1	s_1y_a	$+0.2657$
K_1K_1	s_1z_2	0	K_1K_1	s_1z_a	$+0.1470$
K_1K_1	y_1s_2	-0.0309	K_1K_1	y_1s_a	-0.1869
K_1K_1	y_1y_2	-0.0551	K_1K_1	y_1y_a	-0.1393
K_1K_1	y_1z_2	0	K_1K_1	y_1z_a	-0.1442
K_1K_1	z_1s_2	0	K_1K_1	z_1s_a	-0.1034
K_1K_1	z_1y_2	0	K_1K_1	z_1y_a	-0.1442
K_1K_1	z_1z_2	$+0.0140$	K_1K_1	z_1z_a	$+0.0415$
K_1K_1	x_1x_2	$+0.0140$	K_1K_1	x_1x_a	$+0.1213$
s_1s_1	s_1s_2	$+0.0174$	s_1s_1	s_1s_a	$+0.1665$
s_1s_1	s_1y_2	$+0.0466$	s_1s_1	s_1y_a	$+0.2189$
s_1s_1	s_1z_2	0	s_1s_1	s_1z_a	$+0.1211$
s_1s_1	y_1s_2	-0.0300	s_1s_1	y_1s_a	-0.1644
s_1s_1	y_1y_2	-0.0519	s_1s_1	y_1y_a	-0.1150
s_1s_1	y_1z_2	0	s_1s_1	y_1z_a	-0.1228
s_1s_1	z_1s_2	0	s_1s_1	z_1s_a	-0.0910
s_1s_1	z_1y_2	0	s_1s_1	z_1y_a	-0.1228
s_1s_1	z_1z_2	$+0.0133$	s_1s_1	z_1z_a	$+0.0390$
s_1s_1	x_1x_2	$+0.0133$	s_1s_1	x_1x_a	$+0.1070$
y_1y_1	s_1s_2	$+0.0179$	y_1y_1	s_1s_a	$+0.1664$
y_1y_1	s_1y_2	$+0.0469$	y_1y_1	s_1y_a	$+0.2145$
y_1y_1	s_1z_2	0	y_1y_1	s_1z_a	$+0.1244$
y_1y_1	y_1s_2	-0.0314	y_1y_1	y_1s_a	-0.1717
y_1y_1	y_1y_2	-0.0555	y_1y_1	y_1y_a	-0.1185
y_1y_1	y_1z_2	0	y_1y_1	y_1z_a	-0.1318

Table 23 *(continued)*

$\chi_b \chi_c$	$\chi_d \chi_f$	$(b_1 c_1 \| d_1 f_2)$	$\chi_b \chi_c$	$\chi_d \chi_f$	$(b_1 c_1 \| d_1 f_a)$
$y_1 y_1$	$z_1 s_2$	0	$y_1 y_1$	$z_1 s_a$	−0.0888
$y_1 y_1$	$z_1 y_2$	0	$y_1 y_1$	$z_1 y_a$	−0.1173
$y_1 y_1$	$z_1 z_2$	+0.0132	$y_1 y_1$	$z_1 z_a$	+0.0366
$y_1 y_1$	$x_1 x_2$	+0.0132	$y_1 y_1$	$x_1 x_a$	+0.1040
$z_1 z_1$	$s_1 s_2$	+0.0166	$z_1 z_1$	$s_1 s_a$	+0.1601
$z_1 z_1$	$s_1 y_2$	+0.0443	$z_1 z_1$	$s_1 y_a$	+0.2135
$z_1 z_1$	$s_1 z_2$	0	$z_1 z_1$	$s_1 z_a$	+0.1163
$z_1 z_1$	$y_1 s_2$	−0.0284	$z_1 z_1$	$y_1 s_a$	−0.1423
$z_1 z_1$	$y_1 y_2$	−0.0494	$z_1 z_1$	$y_1 y_a$	−0.1087
$z_1 z_1$	$y_1 z_2$	0	$z_1 z_1$	$y_1 z_a$	−0.1116
$z_1 z_1$	$z_1 s_2$	0	$z_1 z_1$	$z_1 s_a$	−0.0922
$z_1 z_1$	$z_1 y_2$	0	$z_1 z_1$	$z_1 y_a$	−0.1261
$z_1 z_1$	$z_1 z_2$	+0.0135	$z_1 z_1$	$z_1 z_a$	+0.0413
$z_1 z_1$	$x_1 x_2$	+0.0128	$z_1 z_1$	$x_1 x_a$	+0.1012
$x_1 x_1$	$s_1 s_2$	+0.0166	$x_1 x_1$	$s_1 s_a$	+0.1573
$x_1 x_1$	$s_1 y_2$	+0.0443	$x_1 x_1$	$s_1 y_a$	+0.2084
$x_1 x_1$	$s_1 z_2$	0	$x_1 x_1$	$s_1 z_a$	+0.1153
$x_1 x_1$	$y_1 s_2$	−0.0284	$x_1 x_1$	$y_1 s_a$	−0.1532
$x_1 x_1$	$y_1 y_2$	−0.0494	$x_1 x_1$	$y_1 y_a$	−0.1054
$x_1 x_1$	$y_1 z_2$	0	$x_1 x_1$	$y_1 z_a$	−0.1136
$x_1 x_1$	$z_1 s_2$	0	$x_1 x_1$	$z_1 s_a$	−0.0848
$x_1 x_1$	$z_1 y_2$	0	$x_1 x_1$	$z_1 y_a$	−0.1136
$x_1 x_1$	$z_1 z_2$	+0.0128	$x_1 x_1$	$z_1 z_a$	+0.0371
$x_1 x_1$	$x_1 x_2$	+0.0135	$x_1 x_1$	$x_1 x_a$	+0.1073
$K_1 s_1$	$K_1 s_2$	−0.0002	$K_1 s_1$	$K_1 s_a$	−0.0052
$K_1 s_1$	$K_1 y_2$	−0.0007	$K_1 s_1$	$K_1 y_a$	−0.0101
$K_1 s_1$	$K_1 z_2$	0	$K_1 s_1$	$K_1 z_a$	−0.0056
$K_1 y_1$	$K_1 s_2$	−0.0001	$K_1 y_1$	$K_1 s_a$	−0.0007
$K_1 y_1$	$K_1 y_2$	−0.0002	$K_1 y_1$	$K_1 y_a$	−0.0010
$K_1 y_1$	$K_1 z_2$	0	$K_1 y_1$	$K_1 z_a$	−0.0008
$K_1 z_1$	$K_1 s_2$	0	$K_1 z_1$	$K_1 s_a$	−0.0004
$K_1 z_1$	$K_1 y_2$	0	$K_1 z_1$	$K_1 y_a$	−0.0008
$K_1 z_1$	$K_1 z_2$	+0.0000	$K_1 z_1$	$K_1 z_a$	+0.0000
$K_1 x_1$	$K_1 x_2$	+0.0000	$K_1 x_1$	$K_1 x_a$	+0.0005
$s_1 y_1$	$s_1 s_2$	−0.0034	$s_1 y_1$	$s_1 s_a$	−0.0293
$s_1 y_1$	$s_1 y_2$	−0.0078	$s_1 y_1$	$s_1 y_a$	−0.0262
$s_1 y_1$	$s_1 z_2$	0	$s_1 y_1$	$s_1 z_a$	−0.0248
$s_1 y_1$	$y_1 s_2$	+0.0070	$s_1 y_1$	$y_1 s_a$	+0.0484
$s_1 y_1$	$y_1 y_2$	+0.0151	$s_1 y_1$	$y_1 y_a$	+0.0496
$s_1 y_1$	$y_1 z_2$	0	$s_1 y_1$	$y_1 z_a$	+0.0432
$s_1 y_1$	$z_1 s_2$	0	$s_1 y_1$	$z_1 s_a$	+0.0136
$s_1 y_1$	$z_1 y_2$	0	$s_1 y_1$	$z_1 y_a$	+0.0147
$s_1 y_1$	$z_1 z_2$	−0.0019	$s_1 y_1$	$z_1 z_a$	−0.0017
$s_1 y_1$	$x_1 x_2$	−0.0019	$s_1 y_1$	$x_1 x_a$	−0.0142

Table 23 *(continued)*

$\chi_b\,\chi_c$	$\chi_d\,\chi_f$	$(b_1\,c_1\,\vert\,d_1\,f_2)$	$\chi_b\,\chi_c$	$\chi_d\,\chi_f$	$(b_1\,c_1\,\vert\,d_1\,f_a)$
s_1z_1	s_1s_2	0	s_1z_1	s_1s_a	− 0.0162
s_1z_1	s_1y_2	0	s_1z_1	s_1y_a	− 0.0248
s_1z_1	s_1z_2	+ 0.0017	s_1z_1	s_1z_a	+ 0.0050
s_1z_1	y_1s_2	0	s_1z_1	y_1s_a	+ 0.0136
s_1z_1	y_1y_2	0	s_1z_1	y_1y_a	+ 0.0147
s_1z_1	y_1z_2	− 0.0019	s_1z_1	y_1z_a	− 0.0017
s_1z_1	z_1s_2	+ 0.0020	s_1z_1	z_1s_a	+ 0.0314
s_1z_1	z_1y_2	+ 0.0070	s_1z_1	z_1y_a	+ 0.0498
s_1z_1	z_1z_2	0	s_1z_1	z_1z_a	+ 0.0118
s_1z_1	x_1x_2	0	s_1z_1	x_1x_a	− 0.0079
y_1z_1	s_1s_2	0	y_1z_1	s_1s_a	+ 0.0050
y_1z_1	s_1y_2	0	y_1z_1	s_1y_a	+ 0.0062
y_1z_1	s_1z_2	− 0.0006	y_1z_1	s_1z_a	− 0.0002
y_1z_1	y_1s_2	0	y_1z_1	y_1s_a	− 0.0071
y_1z_1	y_1y_2	0	y_1z_1	y_1y_a	− 0.0087
y_1z_1	y_1z_2	+ 0.0010	y_1z_1	y_1z_a	+ 0.0005
y_1z_1	z_1s_2	− 0.0006	y_1z_1	z_1s_a	− 0.0078
y_1z_1	z_1y_2	− 0.0012	y_1z_1	z_1y_a	− 0.0086
y_1z_1	z_1z_2	0	y_1z_1	z_1z_a	− 0.0030
y_1z_1	x_1x_2	0	y_1z_1	x_1x_a	+ 0.0022
s_1x_1	s_1x_2	+ 0.0017	s_1x_1	s_1x_a	+ 0.0187
s_1x_1	y_1x_2	− 0.0019	s_1x_1	y_1x_a	− 0.0142
s_1x_1	z_1x_2	0	s_1x_1	z_1x_a	− 0.0079
s_1x_1	x_1s_2	+ 0.0020	s_1x_1	x_1s_a	+ 0.0239
s_1x_1	x_1y_2	+ 0.0070	s_1x_1	x_1y_a	+ 0.0373
s_1x_1	x_1z_2	0	s_1x_1	x_1z_a	+ 0.0206
y_1x_1	s_1x_2	− 0.0006	y_1x_1	s_1x_a	− 0.0052
y_1x_1	y_1x_2	+ 0.0010	y_1x_1	y_1x_a	+ 0.0078
y_1x_1	z_1x_2	0	y_1x_1	z_1x_a	+ 0.0023
y_1x_1	x_1s_2	− 0.0006	y_1x_1	x_1s_a	− 0.0056
y_1x_1	x_1y_2	− 0.0012	y_1x_1	x_1y_a	− 0.0053
y_1x_1	x_1z_2	0	y_1x_1	x_1z_a	− 0.0050
z_1x_1	s_1x_2	0	z_1x_1	s_1x_a	− 0.0029
z_1x_1	y_1x_2	0	z_1x_1	y_1x_a	+ 0.0023
z_1x_1	z_1x_2	+ 0.0004	z_1x_1	z_1x_a	+ 0.0039
z_1x_1	x_1s_2	0	z_1x_1	x_1s_a	− 0.0031
z_1x_1	x_1y_2	0	z_1x_1	x_1y_a	− 0.0050
z_1x_1	x_1z_2	+ 0.0004	z_1x_1	x_1z_a	+ 0.0009

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